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Kinetics of the Isotopic Exchange Reaction Between Carbon Monoxide and Carbon Dioxide*[1]

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The rate of exchange of the C^{13} isotope between carbon monoxide and carbon dioxide has been studied. It has been found to be a surface catalyzed reaction on quartz, gold, and silver surfaces. Within the limits of experimental error, which are rather large because of change of surface activity, the reaction is independent of pressure and composition of the gas mixture. The exchange is accelerated by hydrogen or water vapor. Oxygen produces a rapid initial exchange attributed to a chain process of oxidation of carbon monoxide, but is without effect on the subsequent exchange. Isotope exchange takes place with a velocity convenient for study around 900°C, and at this temperature the apparent energy of activation is about 100 kcal.

Several mechanisms for the exchange of C^{13} have been examined. One which is not entirely free of difficulties accounts for the experimental data. This assumes the presence of H and OH molecules (or other activated forms of H_2 and H_2O) on the surface with the condition that the total amounts of these molecules is constant.

INTRODUCTION

THE partial separation of the isotopes of carbon and oxygen by Urey and his co-workers[3] has made possible the use of isotopic concentrates of these elements for tracer techniques and for the investigation of the mechanisms of certain exchange reactions.[4] The mass spectrometer was used by Leifer and Urey[5] to follow the course of the decomposition of gaseous dimethyl ether. Using essentially the same technique as that of Leifer and Urey, we have investigated the exchange of C^{13} and O^{18} between carbon monoxide and carbon dioxide. The difference in valence of the carbon in these two compounds would probably lead to the expectation that exchange in the gaseous state would not occur, although such a conclusion could hardly be regarded as certain before experiments have been performed to test this point. The results of the present research show that any such exchange is far slower than heterogeneous processes occurring. It is of interest to study possible relations between this exchange reaction and the important combustion reactions of

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[3] C. A. Hutchison, D. W. Stewart, and H. C. Urey, J. Chem. Phys. **8**, 532 (1940); J. R. Huffman and H. C. Urey, Ind. Eng. Chem. **29**, 531 (1937).

[4] M. Cohn and H. C. Urey, J. Am. Chem. Soc. **60**, 679 (1938); I. Roberts and H. C. Urey, J. Am. Chem. Soc. **60**, 880, 2391 (1938), **61**, 2580, 2584 (1939); G. A. Mills and H. C. Urey, J. Am. Chem. Soc. **61**, 534 (1939), **62**, 1019 (1940).

[5] E. Leifer and H. C. Urey, J. Am. Chem. Soc. **64**, 994 (1942).

carbon monoxide. As observed in other cases, exchanges of isotopic atoms occur between the walls of the vessel and the reacting molecules in ways which indicate that gaseous reactions on solid surfaces are very complex indeed and probably follow no simple unique mechanisms. This exchange occurs at high temperatures where the reactions of the oxides of carbon are known to be complex and predominantly heterogeneous.[6]

EXPERIMENTAL

The apparatus used in making the kinetic measurements was a mass spectrometer of the Bleakney[7] type. By the use of a mass spectrometer, through which gas from the reaction vessel is passed constantly, it is possible to make continuous observation of the change of isotopic ratio in the course of the exchange reaction between carbon monoxide and carbon dioxide. The gas in the mass spectrometer is always being replaced by fresh gas from the reaction vessel since, of course, the mass spectrometer is constantly being exhausted by a large mercury diffusion pump and an oil pump. The pressure of gas required in the mass spectrometer is only about 10^{-5} mm mercury, so that it is possible to use capillary leaks of such size that no perceptible decrease of pressure in the reaction vessel occurs even for runs of five or six hours duration. The several quartz capillaries employed were tested for rate of gas flow before they were sealed into the reaction vessel, and the capillaries were used only if they permitted from 0.05 to 0.10 cc of gas at standard conditions to pass from atmospheric pressure to high vacuum per hour. Since the volume of the reaction vessel was about 30 cc the decrease of pressure during a run was only around 1 percent.

In connection with this method of isotopic analysis, it should be pointed out that the time scale is only relative, so that the zero time for the reactions measured with the mass spectrometer has no meaning. There are two reasons for this. One of these, inherent in the instrument, is due to the fact that it takes a finite time to displace gas which has been in the mass spectrometer previously. Probably the slowest part of the replacement is not due to diffusion of the gas from the vessel, but to the replacement of gas adsorbed on the metal and glass parts of the instrument. The other reason for disregarding a zero of time is that in these experiments, for convenience of assembly of apparatus, the reaction vessel was inserted in the previously heated furnace and then connected to a line leading to the mass spectrometer. Naturally, raising the vessel to the temperature of the furnace took a finite time for which no value of the temperature can be assigned.

For the preliminary work undertaken with the object of finding the approximate conditions under which the exchange reactions would take place, the oxygen isotope was used as a tracer, i.e., carbon dioxide enriched in O^{18} was allowed to react with ordinary carbon monoxide. It was found that exchange of oxygen occurred with a measurable rate, around 900°C, but that when isotopic equilibrium was established between carbon monoxide and carbon dioxide, the number of moles of O^{18} that the carbon monoxide had gained was less than the number of moles of O^{18} that the carbon dioxide had lost. Experiments using carbon dioxide containing twice the ordinary O^{18} concentration heated alone in the quartz vessel to 900°C showed a slow decrease of $CO^{16}O^{18}$, i.e., mass 46, confirming the suspicion that O^{18} was being exchanged with the O^{16} in or on the silica forming the walls of the vessel. Therefore, it was necessary to employ the isotope C^{13} for the kinetic measurements.

The final design of reaction vessel found most satisfactory and used in most of the experiments, is shown in Fig. 1. It was constructed of quartz with a capillary leak made by the following method: quartz tubing of 6-mm internal diameter was heated until it had sealed shut, and during the sealing the two ends were pulled apart slightly so that the inside of the tube at the seal was conical rather than rounded. With the quartz in a fluid state the two ends were drawn apart suddenly to a distance of about six inches. The process resulted in a tapered capillary from which pieces a few mm in length could be broken, and the capillary remaining tested until the proper size of opening was reached. For protecting the capillary against breakage when ex-

[6] B. Lewis and G. von Elbe, *Combustion, Flame and Explosion of Gases* (The Macmillan Company, New York, 1938); N. Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford University Press, New York, 1935).

[7] Walker Bleakney, Phys. Rev. **40**, 496 (1932).

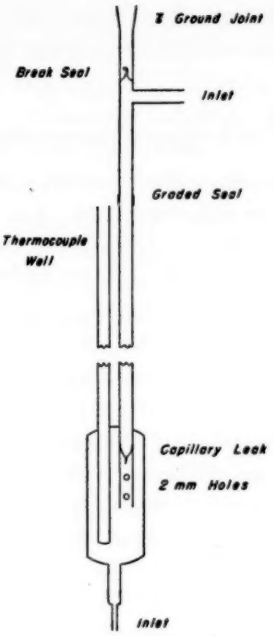

FIG. 1. Reaction vessel.

periments were made with the packed vessel, a protecting tube with a number of 2-mm holes was provided.

The reaction vessel was attached to the system for filling with a gas mixture at two points; the lower opening for filling the reaction vessel itself and the upper side arm for filling above the capillary leak. With the same pressure on both sides of the capillary leak, the gas sample could be permitted to remain in the reaction vessel for any length of time before making the run. The reaction vessel was attached to the mass spectrometer by means of a ground joint. With this design of reaction vessel an auxiliary diffusion pump and oil pump were used to pump out the air above the break seal. The break seal was broken and the gas down to the capillary rapidly pumped off, and then only the gas from the reaction vessel was permitted to enter the mass spectrometer.

The apparatus used for preparing the gas mixtures and filling the quartz reaction vessel consisted of an oil pump and mercury diffusion pump for producing a high vacuum, a McLeod gauge for measuring pressure in the system, carbon monoxide and carbon dioxide gas generators, storage bulbs for pure gases, a mixing bulb with mercury reservoir for transferring gases whenever desired, a gas mixture storage bulb and a mercury manometer, and provision for attaching the reaction vessel for filling. The gases were dried by passing them through a solid carbon dioxide trap. A sample of the gas mixture was taken during the filling process for analysis. A furnace was provided for heating the reaction vessel to 800°C before it was filled with the gas mixture.

The furnace which was used for studying the exchange reaction was made of an alundum cylinder 5 inches in diameter, 12 inches long, which was wound with No. 14 Nichrome V wire in the form of a helix which was covered with alundum cement. In order to equalize the temperature, the windings were divided into several parts each of which was adjustable separately. By the proper adjustment of the various heating currents it was possible to have a temperature uniform to 2–3°C in the working region.

Preparation of Materials

Carbon dioxide enriched in C^{13} was prepared by the combustion of hydrogen cyanide containing about 20 percent C^{13}. The carbon dioxide was bubbled through barium hydroxide and the precipitated barium carbonate was filtered and dried. The dried barium carbonate was placed in the bulb of the gas generator and concentrated sulfuric acid was placed in a side tube with a ground joint connection. The system was pumped out for two hours while the barium carbonate was warmed to expedite the removal of absorbed gases. At the same time the sulfuric acid which was kept cooled with an ice-bath, was freed of dissolved gases. When the stopcock connecting the apparatus to the vacuum system could be closed for five minutes without the pressure in the system building up to more than 1 or 2×10^{-4} mm of mercury, as measured by the McLeod gauge, the materials were considered to be free of foreign gases. Then the sulfuric acid was slowly added to the barium carbonate, and the carbon dioxide produced was passed through a solid carbon dioxide trap and solidified in a tube cooled with liquid nitrogen. Complete removal of moisture was assured by distilling the carbon dioxide six times through a solid carbon dioxide trap at about -100°C with the aid of liquid nitrogen. After this, the carbon

dioxide cooled by liquid nitrogen was evacuated for ten minutes. This procedure removed all foreign gases with the exception of water vapor, which was estimated to be present to the extent of approximately 10^{-5} mm of mercury pressure. The gas was stored in a bulb permanently sealed into the system.

Carbon dioxide enriched in O^{18} was prepared by equilibrating ordinary carbon dioxide with water enriched in O^{18}. The carbon dioxide was prepared from barium carbonate and sulfuric acid. As shown by Mills and Urey,[4] equilibrium in this reaction is reached in a few hours at room temperature.

Carbon monoxide of ordinary isotopic composition was prepared from reagent grade formic acid and sulfuric acid in another gas generator similar to that described for preparing carbon dioxide. The sulfuric acid was cooled with an ice-bath and the formic acid solution, because of its higher vapor pressure, was frozen by a solid carbon dioxide bath. When all dissolved gases had been removed, the sulfuric acid was gradually added to the formic acid, which was allowed to warm to room temperature. The carbon monoxide was passed through two liquid nitrogen traps and stored in a bulb sealed into the system.

Oxygen was prepared by the thermal decomposition of potassium permanganate as suggested by Farkas and Melville.[8] A tube containing a few grams of reagent potassium permanganate was sealed into the system and evacuated to pressure of less than 2×10^{-4} mm of mercury. Then the tube was heated to 250°C with a small flame and the liberated oxygen passed through soda-lime, glass-wool, and a solid carbon dioxide bath. Hydrogen was prepared by purifying tank electrolytic hydrogen.[8] The hydrogen was passed six times, back and forth, through a 12-inch tube of platinized asbestos at 380–400°C. The asbestos was protected by a plug of glass wool and a liquid nitrogen trap. The platinized asbestos was first dried and freed of all volatile material by heating to 400–500°C and pumping off the gases for twenty hours. At the end of this time closing the stopcock to the pump produced a pressure of less than 2×10^{-4} mm of mercury in fifteen minutes with the platinized asbestos at 400°C. The hydrogen was stored in a bulb sealed to the system.

[8] A. Farkas and H. W. Melville, *Experimental Methods in Gas Reactions* (The Macmillan Company, 1939).

Calibration of Apparatus

The principal types of calibration were for temperature and isotope ratio. For the accurate measurement of temperature a platinum -90 percent platinum, -10 percent rhodium thermocouple was employed. The potentiometer used to measure the e.m.f. was calibrated by following the method described by Stein.[9] For calibrating the thermocouple, the ice point, and the melting points of Bureau of Standards samples of tin, zinc, aluminum, and copper, were observed. The procedure was that described by the Bureau of Standards.[10] The error in measuring temperatures is estimated to be $\pm1.0°$.

In order to calibrate the mass spectrometer for use in determining the rate of change of $C^{13}O_2$ and $C^{13}O$ content of the gases, the isotope ratios of ordinary carbon dioxide and ordinary carbon monoxide were measured at the start of every run. This provided a combined correction for both the shunt ratio of approximately 100 to 1 in the amplification of the ion current used in measuring the rare and common isotopes and the incomplete separation of the two peaks which causes the observed magnitude of the rare isotope to be too large.[11] From the observed ratio of masses 44/45 for ordinary carbon dioxide, r_0, the true ratio for ordinary carbon dioxide correcting for O^{17}, R_0, and the observed ratio for an unknown carbon dioxide sample, r_x, the true isotope ratio for the unknown sample, R_x, is calculated from the equation:[12]

$$1/R_x=1/r_x+1/R_0-1/r_0.$$

Procedure for Run

In making a run the first step was the calibration of the shunt ratio and peak separation of the mass spectrometer using ordinary carbon dioxide. Then the C^{13} enriched carbon dioxide in

[9] I. M. Stein, Trans. A.I.E.E. **50**, 1328 (1931).

[10] Kelley, *Pyrometric Practice*, Bureau of Standards Bulletin 170, J. Research Nat. Bur. Stand. **10**, 275 (1933).

[11] M. Cohn and H. C. Urey, reference 4.

[12] This formula is not exact, but the maximum error introduced by its use is less than 1 percent, and is negligible as compared with experimental errors.

the unheated sample tube was frozen and the ordinary carbon monoxide in the tube sampled for calibration. After completing this measurement the remaining carbon monoxide was pumped off and the unheated carbon dioxide allowed to vaporize and pass into the mass spectrometer to determine the initial $C^{13}O_2$ concentration. This order of analysis insured that the gases adsorbed in the mass spectrometer at the start of a run conformed most closely with the gases initially admitted from the reaction vessel.

As soon as the furnace had been brought to the desired temperature, the reaction vessel was inserted and connected to a line containing a three-way stopcock (see Fig. 2). The air in the lines was pumped off, the break-seal broken, and the gases above the capillary leak pumped away. Then the stopcock was turned to admit the gases from the reaction vessel to the mass spectrometer. A solid carbon dioxide trap in this line further cooled with liquid N_2 to $-100°C$ was found advantageous to condense the water vapor in the lines from the vessel to the mass spectrometer; otherwise sufficient water vapor was carried into the mass spectrometer to interfere with the resolution of the 45 from the 44 peak. Even with this trap at $-100°C$ the water vapor peak, mass 18, was usually larger than the carbon dioxide peak, mass 44. The fact that this water originated in the mass spectrometer and in the lines from the reaction vessel to the mass spectrometer rather than in the reaction vessel itself, was indicated by the fact that when the reaction vessel was sealed off in one run, the mass 44 peak decreased rapidly, while the mass 18 peak decreased only very slowly.

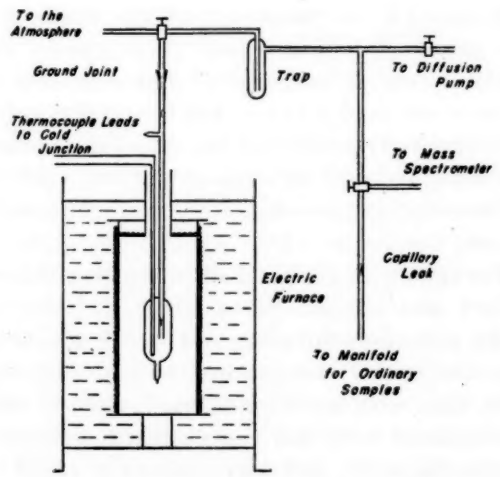

FIG. 2. Reaction vessel—furnace assembly.

Temperature readings were taken every five minutes and the heating current was adjusted when necessary. Temperature was controlled to $\pm 2°C$. In the earlier runs only the carbon dioxide isotopic ratio was measured. In the later runs the isotope ratio of carbon dioxide or carbon monoxide was measured alternately every five minutes. In order to determine the isotope ratio of carbon monoxide in the presence of carbon dioxide, a modification of the method of producing ions was required. The normal electron accelerating potential of 90 volts used in the mass spectrometer not only ionizes carbon dioxide, but also decomposes it to carbon monoxide. To avoid erroneous mass 28/29 ratios for carbon monoxide because of the production of the gas in the mass spectrometer, the electrons were first accelerated by making the first electron accelerating plate 45 volts positive with respect to the filament, and then slowing the beam of electrons after passage through the slit in the first plate by making the second plate negative with respect to the filament.[13] By means of a potentiometer the negative potential between the filament and second accelerating plate was adjusted so that the electrons could be slowed down sufficiently to prevent the decomposition of carbon dioxide, but so that the electrons had sufficient energy to ionize carbon monoxide entering the mass spectrometer from the reaction vessel. With 45-volts accelerating potential, about 25 volts decelerating potential was required.

Preparation of Reaction Surfaces

When it was discovered that reaction took place principally on the quartz surface and with a rate dependent upon the previous treatment of the surface, it was necessary to work out a method of treating the surface to give it approximately the same degree of activity for every run. The procedure which was found satisfactory to condition the vessel was essentially as follows:

The reaction vessel when in place for filling

[13] See reference 7, Fig. 1.

TABLE I. Tabulated data on rate of exchange of C^{13}.

Run no.	Percent CO	Percent CO_2	Pressure in mm of mercury reduced to standard conditions	Temperature °C	Nature of packing	Rate constant $k \times 10^2$ min.$^{-1}$ CO_2	Rate constant $k \times 10^2$ min.$^{-1}$ CO
30	52	48	63	916		0.81	
31	52	48	81	901		0.52	
33	52	48	34	898		0.43	
38	79	21	65	896		0.77	
39	79	21	65	896	Quartz	2.22	
40	79	21	64	870	Quartz	1.48	
41	79	21	64	868		0.22	
42	79	21	22	868		0.29	
43	79	21	64	869	Gold	1.98	
44	79	21	64	868	Silver	1.55	
45	79	21	64	896	Silver	1.48	
46	79	21	63	869	Silver	0.94	
47	79	21	22	896		0.40	
48	79	21	22	868		0.12	
51	84	16	36	898		0.30	
52	84	16	11	898		0.14	
54	84	16	31 (Includes 0.3 mm O_2)	899		0.27 (Final rate)	
55	84	16	13	914		0.48	
61	90	10	25	918	Quartz	0.87	
62	90	10	25	920	Quartz	0.49	
63	90	10	25	921		0.38	
64	90	10	26	920		0.32	
65	90	10	10	918			0.25
66	90	10	12	898		0.12	0.12
67	90	10	9	916			0.30
68	13	87	36	898		0.38	0.45
69	13	87	14	898			0.50
70	13	87	37	917			0.88
71	30	70	34	899		0.33	0.29
72	56	44	34	898		0.32	0.28
73	56	44	34	915		0.49	0.48
74*	82	18	36	914		0.34	0.22
75*	82	18	35	898		0.36	
				914		0.80	
76	82	18	42 (28 mm CO+CO_2) (14 mm H_2)	898		2.4	2.0
77	CO_2^{18} only		40	915–950		0.068	
78	82	18	35 (Includes 4 mm H_2O)	898		2.6	1.7
79	82	18	61	900	Quartz	0.70	0.70
80	82	18	25 (20 mm CO+CO_2) (5 mm H_2)	897	Quartz	1.01	0.85
81	82	18	10	898	Quartz	0.35	0.27
82	82	18	12	897	Quartz	0.29	0.24
83	82	18	11	897	Quartz	0.22	0.21
84	13	87	9	899	Quartz	0.52	0.41
85	82	18	11	898	Gold	6.2	5.4
86	82	18	21 (Includes 0.8 mm O_2)	898		0.33	0.53
87	82	18	11 (8 mm CO+CO_2) (3 mm H_2	898		0.64	0.63
88	82	18	27	866	Gold	0.99	0.97
90	82	18	9	863	Gold	0.58	0.44
91	82	18	29	865	Gold	0.53	0.58
92	77	23	29	864	Gold	0.80	0.72
				879	Gold	1.34	
93	31	69	24	864	Gold	0.81	0.83
94	31	69	10	865	Gold		0.80
95	82	18	33	869	Gold	0.94	1.14
96	82	18	32	885	Gold	1.40	1.52
97	92	18	23 (16 mm CO+CO_2) (7 mm H_2)	899	Gold	3.5	2.5
98	55	45	12	865	Gold	0.79	0.70
99	55	45	48	865	Gold	0.81	0.86
102	91.5	8.5	31	866	Gold	1.97	2.04
104	91.5	8.5	29	650		0.009	0.009

* Between runs 74 and 75 the vessel was cleaned with hot nitric acid and with hot 10 percent hydrofluoric acid to remove the devitrified surface layer of the quartz.

with a gas mixture was surrounded with a small resistance furnace mentioned above, capable of being heated to 800°C.[14] Gases from the previous run and from the sealing operation were removed first by heating to at least 700°C, and pumping to a pressure of 1×10^{-4} mm of mercury, followed by admitting air to a pressure of a few hundred mm of mercury while heating to 750°C, for at least ten minutes, and finally by pumping off the air to a pressure of 1×10^{-4} mm of mercury for thirty minutes. The furnace was turned off while pumping continued and the vessel was allowed to cool below 500°C at which time the reaction mixture was introduced.

This procedure was followed exactly for the earlier runs through run 55, for the later runs from 87 on, and in runs 82 and 83. In run 67, oxygen was introduced to condition the surface.

In the remaining runs, 61 through 86, after the treatment with air, hydrogen was admitted at 5–10 mm pressure with the vessel at a temperature of about 750°C for ten minutes and then pumped off for at least forty-five minutes with the vessel heated to 750–800°C. At the end of this period if the pressure with the stopcock to the pump closed increased to no more than 1×10^{-4} mm of mercury in ten minutes, the furnace was cooled below 500°C and the sample introduced. Treatment of the vessel surface with hydrogen reduced to some extent the variation of the catalytic activity of the surface from run to run.

For runs with gold and silver packing the procedure was similar. Sheet silver was cut into strips to fit into the tube, and after introduction into the vessel was washed with dilute nitric acid, then with water, and dried. Gold in strips was washed with hot concentrated nitric acid, then with water, and dried. After the vessel was attached to the system it was treated with air

[14] Y. Kondo and O. Toyama, Rev. Phys. Chem. Japan **13**, 166 (1939), in a study of the oxidation of carbon monoxide above the upper explosion limit were able to obtain reproducible results only when the vessel was heated to 750–800°C, and evacuated between runs.

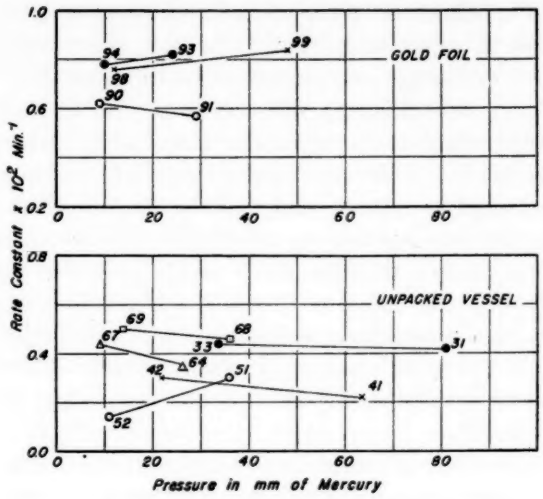

FIG. 3. Pressure *vs.* rate of exchange.

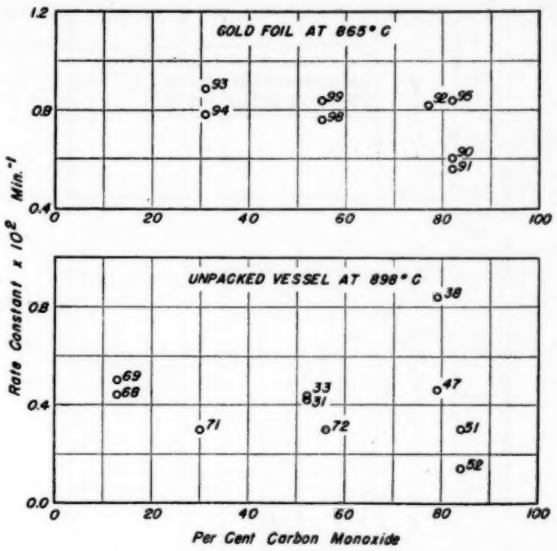

FIG. 4. Composition of gas *vs.* rate of exchange.

and in some cases with hydrogen, as described previously.

RESULTS

A total of 104 runs was made. Except for the preliminary runs with O^{18} tracer, and a number of runs where difficulty was experienced with contamination of the samples or trouble with the mass spectrometer, all data are presented in an abbreviated form in Table I. The rate constants reported were calculated from the slope of the curve obtained by plotting the logarithm of the difference between the mole fraction of C^{13} in carbon dioxide or in carbon monoxide at any time, and the mole fraction at infinity, i.e., at equilibrium, against the time. As has been shown previously[15] this must of necessity give a straight line for all isotopic exchange reactions. In general, the mass spectrometer data yielded good linear curves.

The effects on rate of exchange of several variables were studied; namely, temperature, composition of the gas mixture, total pressure of the gas mixture, quartz packing, other types of surfaces, and small amounts of other gases. Only one variable was altered at a time. In Fig. 3 several curves are presented showing the effect of varying the total pressure of the gas mixture only. No significant trend of reaction rate with pressure is indicated in the range from 10 to 80 mm of mercury total pressure. It is difficult to reproduce a surface and to eliminate the effect of adsorption in the mass spectrometer, particularly at low pressures, and thus a small positive or negative slope has no significance. In a few cases, rate constants were corrected for the difference of one or two °C between runs.

In Fig. 4 data are given attempting to relate reaction rate with composition of the gas mixture, all other variables being maintained as

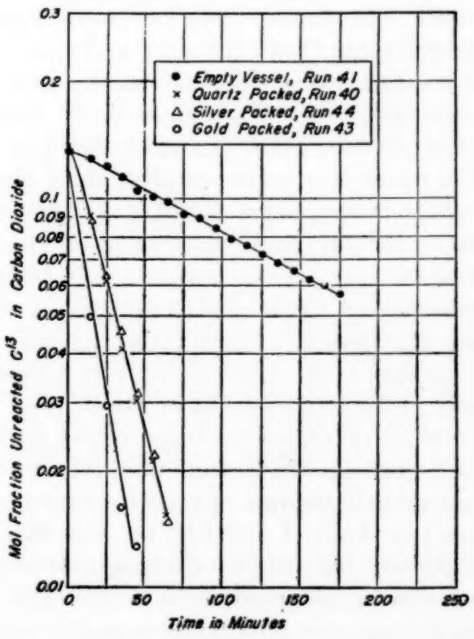
Empty Vessel, Run 41
Quartz Packed, Run 40
Silver Packed, Run 44
Gold Packed, Run 43
Mol Fraction Unreacted C¹³ in Carbon Dioxide
Time in Minutes

FIG. 5. Rate of exchange on various surfaces at 869°C.

[15] H. A. C. McKay, Nature **142**, 997 (1938).

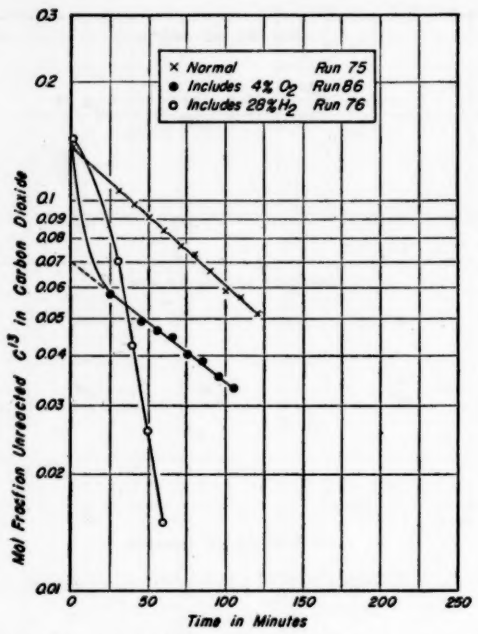

FIG. 6. Effect of hydrogen and oxygen on the rate of exchange at 898°C.

uniform as possible. Here also, within the limits of error, there is no significant change of rate of isotope exchange with composition.

In Table I and in Fig. 5 the effect of increasing the surface of the vessel by packing with quartz tubing is shown. There is a marked increase in rate of exchange when the quartz surface is increased. The surface was increased approximately to three times the area and there is a fairly good parallelism between surface and rate as indicated by the data. The catalytic effect of gold and silver surfaces of known area was also studied. Gold is a better catalyst than quartz, and silver is as good a catalyst as quartz, as shown by the data and Fig. 5. Data for the rate of reaction on a gold surface are about as reproducible as for a quartz surface. A silver surface decreases in activity rather rapidly, possibly because of the appreciable vapor pressure of silver at the temperatures involved.

The effect of adding hydrogen to the reaction mixture up to one-third of the total mixture is to increase greatly the rate of exchange on a quartz surface (see Table I and Fig. 6). The effect of hydrogen on the rate of exchange on a gold surface is not at all pronounced. Water vapor like hydrogen catalyzes the carbon monoxide-carbon dioxide exchange on quartz.

The effect of a few percent of oxygen is to cause a rapid immediate exchange, but then a final exchange not significantly different from normal (see Fig. 6). Obviously at the furnace temperature the oxygen combines with carbon monoxide. However, the immediate isotope exchange is greater than can be accounted for by oxidation of carbon monoxide, as the curve extrapolated to zero time yields a value for $(X-X_\infty)$ of about 0.07 while the value would only be expected to be reduced to 0.103. Therefore, reaction chains of some length which produce considerable isotope exchange, may be involved.

The effect of temperature on the rate of isotope exchange is shown by the data in Tables I and II. It is evident that the temperature coefficient of the reaction is quite large. The apparent energies of activation at various compositions and pressures on several surfaces are reported in Table II, for runs where the surfaces were as nearly identical as possible. It is evident that energy of activation does not depend upon pressure or composition, but is indicated to be slightly lower on a gold than on a quartz surface.

Several runs were made which are discussed at some length below under "Discussion," to determine whether carbon dioxide could be formed from carbon monoxide. The results in Table III, for run 103, showed that there was a slow reaction to form the equilibrium concentration of carbon monoxide and carbon dioxide, and reaction was found to begin at a relatively low temperature.

If the rate of attainment of equilibrium in the reaction $2\,CO \rightleftarrows CO_2 + C$ is of the same order of

TABLE II. Apparent energies of activation.

Percent CO	Total pressure in mm of mercury	Surface	Apparent energy of activation	Run no.
82	35	Quartz	138 kcal.	75A, 75B
79	65	Quartz	119	38, 41
79	22	Quartz	114	47, 48
90	11	Quartz	101	65, 66
13	37	Quartz	107	68, 70
52	72	Quartz	91	72, 73
			Av. 112 a.d. = ±12	
82	33	Gold	61	95, 96
77	29	Gold	88	92A, 92B
			Av. 75 a.d. = ±14	

magnitude as the rate of isotope exchange, then the straight lines obtained by plotting the data for carbon exchange should not extrapolate back to the zero value obtained on the unheated gas mixture. It was found that not all individual curves could be extrapolated to zero, but analysis of the data by classifying the runs according to pressure or composition or speed of reaction in no case gave an average extrapolated zero significantly different from the zero of the original unheated sample. This is an indication that the isotope exchange reaction is probably not complicated by concurrent elementic reactions.

In run 77 the rate of decrease of O^{18} from carbon dioxide heated alone in the quartz reaction vessel was studied. A very slow exchange of O^{18} with the silica was indicated by the decrease of mass 46, and this exchange was found to be almost independent of temperature, which indicates that the transfer of oxygen atoms through the silica may be the slow step in this exchange of oxygen between carbon dioxide and quartz.

DISCUSSION

The outstanding features of the results with which any theory must be in accord are as follows: (1) the exchange is independent of pressure and of composition of the gas mixture; (2) the exchange is largely if not entirely heterogeneous, taking place on a quartz, gold, or silver surface; and (3) the apparent energy of activation of the exchange reaction is very large, being of the order of 100 kcal.

A number of mechanisms have been considered for the exchange of C^{13} between carbon monoxide and carbon dioxide. The first mechanism will be presented in detail to illustrate the method of derivation.

Mechanism I

The first reaction mechanism to be considered is the direct transfer of an oxygen atom from carbon dioxide to carbon monoxide, thus

$$OC^{13}O+C^{12}O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C^{13}O+OC^{12}O.$$

For this process the rate of disappearance of $C^{13}O_2$ is obtained from the difference in the rates of the forward and reverse reactions, by the equation

$$-d(C^{13}O_2)/dt=k_1(C^{13}O_2)(C^{12}O) \\ -k_{-1}(C^{12}O_2)(C^{13}O).$$

Now for $(C^{13}O_2)$, the atom fraction of C^{13} in carbon dioxide, x, can be substituted, thus

$$(C^{13}O_2)=x(CO_2).$$

And for $(C^{13}O)$ the atom fraction of C^{13} in carbon monoxide, y, can be substituted

$$(C^{13}O)=y(CO).$$

Whence,

$$-(CO_2)\frac{dx}{dt}=k_1(CO_2)(CO)x(1-y) \\ -k_{-1}(CO_2)(CO)y(1-x).$$

For all practical purposes the rates of the forward and reverse reactions are identical, so that $k_1=k_{-1}$ and

$$-\frac{dx}{dt}=k_1(CO)(x-y).$$

The total C^{13} is constant throughout the reaction; therefore, the concentration of C^{13} in carbon monoxide and carbon dioxide at any time is related to the concentration at infinity (equilibrium) by the expression,

$$[(CO_2)+(CO)]x_\infty=x(CO_2)+y(CO),$$

or, rearranged so that y can be given in terms of x alone,

$$y=x_\infty-(x-x_\infty)(CO_2)/(CO).$$

TABLE III. (Data from Run 103.) Pure carbon monoxide in reaction vessel at 36 mm of mercury pressure.

Time—Hours	Temperature—°C	Mass spectrometer reading of the ratio of masses 28/44 (CO/CO_2)
0	30	180
1	460	200
2	570	170
3	680	123
4	750	89
5	820	81
6	890	71
6½	905	70

Substituting above, the equation becomes

$$-dx/dt=k_1(x-x_\infty)[(CO_2)+(CO)].$$

Obviously, the rate of disappearance of C^{13} is independent of the composition of the gas mixture, but directly dependent upon the pressure.

Mechanism II

The previous mechanism was modified to take into account a reaction proceeding on the surface, thus,

$$C^{13}O_2(s)+C^{12}O(s)\rightleftarrows C^{12}O_2(s)+C^{13}O(s).$$

Various degrees of adsorption were tested using the Langmuir adsorption equation without yielding an expression independent of both pressure and composition. Incidentally, adsorption measurements on quartz surfaces by Hartley, Henry, and Whytlaw-Gray[16] reveal rather weak adsorption of about the same magnitude for carbon monoxide, carbon dioxide, and oxygen.

Mechanism III

Another possible mechanism involved the dissociation of carbon dioxide,

$$2\ CO_2\rightleftarrows 2\ CO+O_2,$$

for which the equilibrium constant is

$$K_{1200^\circ}=3.27\times10^{-16}$$

according to Kassel.[17] The equilibrium concentration of oxygen is so small by this process that it does not seem a likely mechanism for the exchange. If the reaction is considered to be

$$CO_2\rightleftarrows CO+O,$$

the additional energy required to dissociate oxygen molecules must be allowed for, which makes this mechanism even more unlikely. Moreover, if the dissociation of carbon dioxide is considered to occur on the surface, a suitable expression for the reaction rate is not obtained.

Mechanism IV

In this case the slow process was assumed to be the adsorption or desorption of one of the reactants although the high apparent energy of activation for the isotopic exchange makes it improbable that adsorption is rate-controlling. Here, again, the required independence of pressure and composition of the gas mixture was not achieved in the resulting equations.

Mechanism V

Another mechanism for exchange which can be postulated involves the reduction of silica by carbon monoxide. The reduction of quartz by carbon monoxide has been observed according to Sosman[18] to occur only at 1350° and higher temperatures; consequently reaction at the temperatures in question must be extremely limited. However, the observed exchange of O^{18} between silica and carbon dioxide indicates that a carbon-oxygen bond can be broken on a quartz surface. The mechanism can be written

$$C^{13}O+SiO_2\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}C^{13}O_2+SiO.$$

However, the resulting rate equations do not satisfy the conditions imposed by the data.

Mechanism VI

Another mechanism which has been considered involves the reaction,

$$2\ CO\rightleftarrows C+CO_2.$$

In run 103 (Table III) it was shown that this reaction takes place at the temperatures of our experiments. However, the pressure of the gas mixture and the percent of carbon monoxide was not sufficiently high in any exchange experiment to cause deposition of massive carbon on the walls of the vessel. This is illustrated by the following calculation for the most favorable case, run 102. The apparent equilibrium constant for this case would be

$$[CO]^2/[CO_2]=1.67.$$

[16] G. A. R. Hartley, T. H. Henry, and R. Whytlaw-Gray, Trans. Faraday Soc. **35**, 1452 (1939).
[17] Kassel, J. Am. Chem. Soc. **56**, 1838 (1934).
[18] R. B. Sosman, *Properties of Silica* A.C.S. Monograph No. 37 (Chemical Publishing Company, Brooklyn, New York).

Since the equilibrium constant for the reaction at this temperature is about 20, according to Kassel,[17] it is obvious that under the conditions of the exchange study no more than a monomolecular film of carbon could be laid down. It is noteworthy that Rhead and Wheeler[19] observed both the forward and reverse reactions to be first order, and concluded that they were surface phenomena. Furthermore, Morita and Titani[20] in a study of the exchange of O^{18} between oxygen and water and between oxygen and carbon dioxide, found the process to be heterogeneous proceeding on platinum at 550°C and on quartz slightly at 800°C.

Just as before, let x = mole fraction $C^{13}O_2$,
y = mole fraction $C^{13}O$,
z = mole fraction C^{13}.

Setting up the three differential equations and solving as before, one finds that the solutions are

$$x = C_{1x}e^{At} + C_{2x}e^{Bt} + C_{3x},$$
$$y = C_{1y}e^{At} + C_{2y}e^{Bt} + C_{3y},$$
$$z = C_{1z}e^{At} + C_{2z}e^{Bt} + C_{3z},$$

where

$$A, B = \frac{-(ab+2ac+bc) \pm (b^2c^2+2ab^2c+a^2b^2+4a^2c^2)^{\frac{1}{2}}}{2abc}.$$

$$a = \frac{(CO_2)}{k_1(CO_2)(C)},$$

$$b = \frac{(CO)}{k_1(CO_2)(C)},$$

$$c = \frac{(C)}{k_1(CO_2)(C)}.$$

The C's are to be determined from the boundary conditions. The exact solution of these expressions for exchange by means of carbon monoxide dissociation is unfortunately too complicated to permit exact determination of the relationship of pressure and composition to rate of exchange. Several approximate solutions of these differential equations have been considered but no reasonable assumption has been found to give an expression for rate of exchange independent of total pressure and of composition of the gas mixture.

Meyer[21] claims that the reaction $CO_2+C \rightarrow 2\,CO$ is zero order with an energy of activation of 90 kilocalories. This is in general agreement with the findings of this investigation, as is the observation of Titani and Morita[20] that the O^{18} exchange is independent of the composition of the oxygen-carbon dioxide mixture.

Mechanism VII

The effect of hydrogen or water vapor in accelerating the exchange of C^{13} may be attributed to the reaction:

$$CO_2 + H_2 \rightleftarrows CO + H_2O.$$

According to Kassel the equilibrium constant for this reaction is about unity at the temperatures concerned, so that where considerable quantities of hydrogen or water vapor were introduced, the acceleration of the exchange reaction may have been caused by this reaction predominating. Hinshelwood[22] reported that above 800°C the direct water gas reaction becomes important in the oxidation of carbon monoxide. Also, in the case of the exchange reaction with hydrogen, the reaction is complicated by surface phenomena. The gaseous reaction as written above does not give the observed independence of pressure and composition.

At this point Professor H. S. Taylor pointed out that hydrogen and water are adsorbed strongly on quartz at the temperatures of our experiments.[23] Accordingly we have tried the mechanism,

$$C^{13}O_2 + H \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C^{13}O + OH,$$

where we assume that H and OH are adsorbed on the surface. The kinetic equation is then

$$-\frac{d(C^{13}O_2)}{dt} = k_1(C^{13}O_2)(H) - k_{-1}(C^{13}O)(OH),$$

[19] T. F. E. Rhead and R. V. Wheeler, J. Chem. Soc. 2178 (1910); 461 (1912).
[20] N. Morita and T. Titani, Bull. Chem. Soc. Japan **13**, 357, 601 (1938).
[21] L. Meyer, Trans. Faraday Soc. **34**, 1056 (1938).
[22] C. N. Hinshelwood, Proc. Roy. Soc. **A137**, 87 (1932).
[23] H. N. Alyea, J. Am. Chem. Soc. **53**, 1324 (1931).

whence,

$$-(CO_2)\frac{dx}{dt}=k_1(CO_2)(H)(x-y).$$

Using the equation

$$(CO_2)x+(CO)y=\{(CO_2)+(CO)\}x_\infty,$$

we secure

$$-\frac{dx}{dt}=k_1(H)\frac{(CO_2)+(CO)}{(CO)}(x-x_\infty),$$

and again the observed rate constant should vary with pressure and composition. However, we can make an assumption in regard to the relative amounts of H and OH on the surface. If we assume that

$$(H)+(OH)=C_1, \text{ a constant,}$$

and use the equilibrium equation

$$\frac{(CO)(OH)}{(CO_2)(H)}=K,$$

we can eliminate both (OH) and (H) from the kinetic equation. This gives

$$-\frac{dx}{dt}=k_1C_1\frac{(CO_2)+(CO)}{K(CO_2)+(CO)}(x-x_\infty).$$

Thus we see that the constant becomes independent of pressure and composition if $K\sim1$, and this means that the ratio (H)/(OH) on the surface is equal to (CO)/(CO_2) in the gas phase. To account for the increased exchange rate when hydrogen or water is added, we must assume that the surface at the low pressures of hydrogen and water vapor is covered to a small extent with hydrogen atoms or OH groups. On the other hand, it is difficult to find any reasonable justification for the assumption that (H)+(OH)=C except that the surface is completely covered by these molecules. Finally, we must assume a similar behavior for a gold surface as for quartz.

It should be noted that the following mechanism

$$H_2\rightleftarrows H_2^*$$

$$C^{13}O_2+H_2^*\rightleftarrows C^{13}O+H_2O^*$$

$$H_2O^*\rightleftarrows H_2O,$$

with the condition that

$$(H_2^*)+(H_2O^*)=C,$$

is also in agreement with the data with the same difficulties encountered in the assumption of H and OH molecules on the surface, and is, in fact, only a more general statement of the same mechanism.

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Deswelling of Gels by High Polymer Solutions

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When a cross-linked polymer initially swelled to its equilibrium volume in pure solvent is transferred to a solution of a high polymer in the same solvent and at the same temperature, the gel deswells. A quantitative treatment of this effect is given in terms of the Flory-Rehner theory of the thermodynamic properties of gels, and the Flory-Huggins theory of thermodynamics of high polymer solutions. The extent of deswelling depends on the molecular weight and concentration of the solute, on the solvent-polymer interactions, and on the degree of cross-linking in the gel. It thus offers in principle a new method for determination of the number average molecular weight of the solute. Various calculations are presented to show the extent of deswelling under given conditions. Finally, some experimental data is offered to demonstrate determinations of molecular weights, using styrene-divinylbenzene copolymer gels and polystyrene solutions.

INTRODUCTION

IT is well known that when certain high molecular weight materials are placed in a suitable solvent they swell to an equilibrium value determined by the solvent, the temperature, and the nature of the polymer. These polymers belong to two general types: (a) linear polymers which swell to a limited extent in one solvent but which can dissolve if the solvent and/or the temperature is suitably chosen; (b) three-dimensional polymers whose maximum swelling is limited by a primary valence network. An example of the type (a) is gelatin whose equilibrium swelling characteristics first received a rational explanation by Proctor and Wilson.[1] Haller[2] has discussed swelling pressure as a function of energy and entropy changes on dilution. Gee[3] has furnished a theory for equilibrium swelling based on entropy and heat of mixing effects. More recently Tobolsky[4] has treated the process of dissolution or "melting" of these soluble gels.

Frenkel[5] proposed that equilibrium swelling for three-dimensional gel structures occurs when the osmotic pressure is equal to the elastic reaction of the network chains. Flory and Rehner[6] then provided a mathematical formulation for Frenkel's fundamental idea in terms of modern concepts of the thermodynamic behavior of high polymer systems. They included both the entropy and the heat of mixing effects. In particular, they showed that the activity, a_{1g}, of the solvent within the gel is given by

$$\ln a_{1g}=\mu_g v_{2g}^2+\ln(1-v_{2g})+v_{2g}+(\rho V_1/M_c)(v_{2g})^{\frac{1}{3}}, \quad (1)$$

where v_{2g} is the volume fraction of polymer in the swollen gel, ρ is the density of the polymer, V_1 is the molar volume of the solvent, M_c is the molecular weight of the polymer between points of cross-linkage, and μ_g is the constant providing for interaction between polymer and solvent. This notation is similar to that employed by Flory and Rehner except for the subscript g which is used to identify the gel phase, and for the substitution of μ_g in place of their $K/2$. μ_g is used here in keeping with Huggins' μ_1 constant[7] to represent the polymer-solvent interaction term for soluble polymer systems. Flory and Rehner state that equilibrium swelling of a three-dimensional gel occurs when the partial molal free energy of dilution, $\Delta\bar{F}_1$, is zero, and hence when

$$M_c=-\rho V_1(v_{2g^0})^{\frac{1}{3}}/[\mu_g v_{2g^0}^2+\ln(1-v_{2g^0})+v_{2g^0}], \quad (2)$$

v_{2g^0} is now the volume fraction of polymer in the swollen gel which is in equilibrium with pure solvent. Since v_{2g^0} can be measured experi-

[1] H. R. Proctor and J. A. Wilson, J. Chem. Soc. **109**, 307 (1916).
[2] W. Haller, Kolloid Zeits. **56**, 262 (1931).
[3] G. Gee, Trans. Faraday Soc. **38**, 276, 418 (1942); I.R.I. Trans. **18**, 266 (1943).
[4] A. Tobolsky, J. Chem. Phys. **11**, 290 (1943).
[5] J. Frenkel, Acta Physicochim. **9**, 235 (1938); Rub. Chem. Tech. **13**, 264 (1940).
[6] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. **11**, 521 (1943).
[7] M. L. Huggins, Ann. N. Y. Acad. Sci. **44**, 431 (1943).

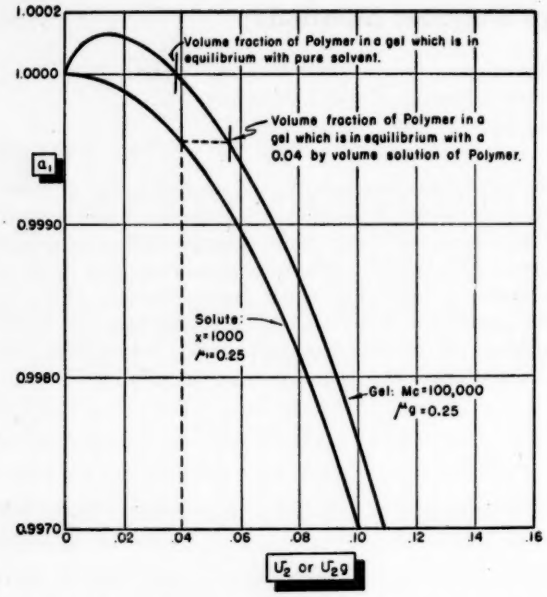
1.0002
1.0000
0.9990
0.9980
0.9970
a_1
Volume fraction of Polymer in a gel which is in equilibrium with pure solvent.
Volume fraction of Polymer in a gel which is in equilibrium with a 0.04 by volume solution of Polymer.
Solute: x=1000 μ_1=0.25
Gel: Mc=100,000 μ_g=0.25
0 .02 .04 .06 .08 .10 .12 .14 .16
U_2 or U_{2g}

FIG. 1. Dependence of solvent activity, a_1 (or a_{1g}), on volume fraction, v_{2g}, of network polymer (upper curve); and on volume fraction, v_2, of solute (lower curve).

mentally on a given sample, and since μ_g can be determined from swelling values at several temperatures, it is thus possible to calculate the extent of cross-linking as expressed by M_c. M_c is, therefore, a characteristic constant for a given gel sample while μ_g is unique for a fixed gel-solvent system at a given temperature. μ_g accounts for the variation in equilibrium swelling volume with different types of solvents and with temperature. Staudinger, Heuer, and Husemann[8] have reported numerous results on the swelling of styrene-divinylbenzene copolymers in a variety of solvents. Their results attest to the importance of μ_g term in Eq. (1), as well as offering qualitative confirmation of the numerical relationship involved.

The cross-linking agent used throughout this report consisted of the three isomers of divinylbenzene diluted with the three isomers of ethylvinylbenzene. This mixture usually contained from 30 to 40 percent of divinylbenzene, with the meta-isomer predominating. Huggins[7] has calculated μ_1 for toluene-polystyrene solutions to be 0.44, and we assume that μ_g is also 0.44, when toluene is used for styrene-divinyl benzene gels. The validity of this assumption must still be justified by some experiments to determine how nearly μ_g is the equivalent of μ_1. Alfrey and coworkers[9] have shown, for example, that μ_1 for toluene-polystyrene varies with the temperature at which the styrene was polymerized. It may be that the presence of traces of cross-linking agents will alter the significance of this interaction constant, even when the cross-linking agent is chemically similar to the main polymer constituent. The principal cause for a difference between μ_1 and μ_g is probably the restrictions imposed on the possible number of configurations due to cross-links. This effect is likely small for a slightly cross-linked gel.

[8] H. Staudinger, W. Heuer, and E. Husemann, Trans. Faraday Soc. **32**, 323 (1936).

DESWELLING OF GELS BY HIGH POLYMER SOLUTIONS

There is now an interesting consequence of the swelling phenomena outlined above. If a swollen gel in equilibrium with pure solvent is transferred to a solution of a high polymer in the same solvent and at the same temperature, the gel will deswell. The polymer in solution prefers to be in a more diluted state and can do so only by extracting solvent from the swollen gel. The elastic contraction of the network chains within the gel assists in this process until a new swelling equilibrium obtains. The extent of deswelling will depend primarily on the degree of cross-linking in the gel, on the concentration and

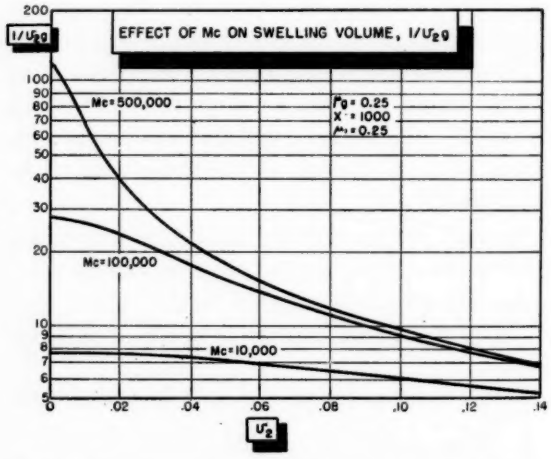

FIG. 2. Decrease in swelling volume, $1/v_{2g}$, with increasing amounts of solute, v_2, for three gels of different degrees of cross-linking.

[9] T. Alfrey, A. Bartovics, and H. Marks, J. Am. Chem. Soc. **65**, 2321 (1943).

molecular weight of the dissolved polymer, and on the solvent-polymer interactions, as expressed by μ_g and μ_1. As one example, a styrene −0.05 percent divinylbenzene gel which had swelled to 13.8 its dry volume in pure toluene, decreased to 7.7 times its dry volume in a 10 percent by weight solution of polystyrene in toluene. The polystyrene solute had a molecular weight of 302,000 by light scattering.[10] Other examples of the extent of deswelling will be apparent later.

After we had observed such deswelling action, a survey of the literature revealed that this behavior was quite well known. In fact, Blow and Stamberger[11] in their classical investigation of the deswelling of rubber gels, referred to it as the so-called *Bodenkörper* effect, apparently in allusion to earlier work by Ostwald on gelatin. They interpreted this general effect qualitatively on the basis of osmotic pressure, but did not give a quantitative treatment. More recently, Powers and Robinson[12] observed that the swelling of synthetic rubbers by oil was smaller in oils which contained polyisobutylene as a viscosity index stabilizer.

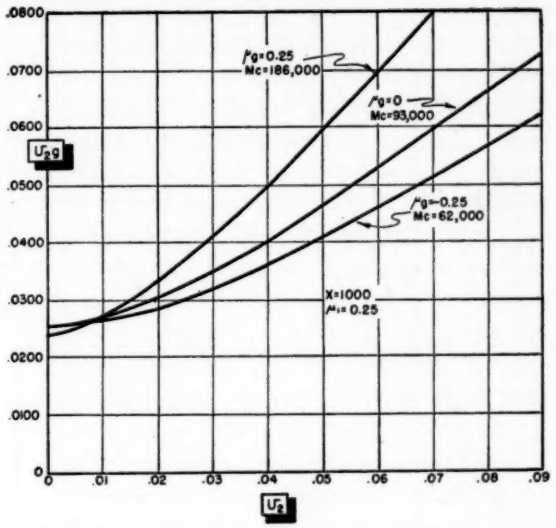

FIG. 4. Dependence of v_{2g} on v_2 for three gels of different M_c and μ_g having approximately the same degree of swelling in pure solvent.

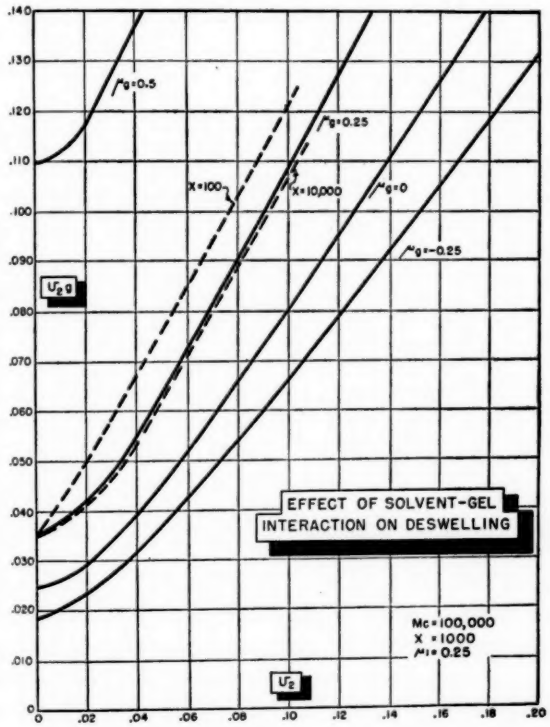

FIG. 3. Increase in network polymer concentration, v_{2g}, with increasing solute concentration, v_2, for different values of μ_g. The upper and lower dashed curves (with $\mu_g=0.25$) illustrate the effect of a very low and a very high molecular weight solute.

Because of current advances in theoretical knowledge concerning the thermodynamics of high polymer systems, it is now relatively simple to provide a quantitative treatment for this dewelling action. It suffices merely to correlate the Flory-Rehner[6] theory of gels with the Huggins[13–15] and Flory[16] treatment of high polymer solutions. Huggins and Flory have shown that the activity of the solvent in contact with solute is given by

$$\ln a_1=\ln(1-v_2)+(1-1/x)v_2+\mu_1 v_2^2, \qquad (3)$$

where v_2 is the volume fraction of polymer in solution, and x is the ratio of the volume of a polymer molecule to the volume of a solvent molecule. Flory[16d] has demonstrated that this equation is also valid for a heterogeneous solute if x is replaced by its number average value $\bar{x}_n$.

The criterion for the new swelling equilibrium

[10] P. Debye, J. App. Phys. **15**, 338 (1944); P. M. Doty, B. H. Zimm, and H. Mark, J. Chem. Phys. **13**, 159 (1945).
[11] C. M. Blow and P. Stamberger, Rec. Trav. Chim. **48**, 681 (1929).
[12] P. O. Powers and H. A. Robinson, Ind. Eng. Chem. **34**, 614 (1942).
[13] M. L. Huggins, Ann. N. Y. Acad. Sci. **43**, 1 (1942).
[14] M. L. Huggins, J. Phys. Chem. **46**, 151 (1942).
[15] M. L. Huggins, J. Am. Chem. Soc. **64**, 1712 (1942).
[16] P. J. Flory, J. Chem. Phys. (a) **9**, 660 (1941); (b) **10**, 51 (1942); (c) **12**, 114 (1944); (d) **12**, 425 (1944).

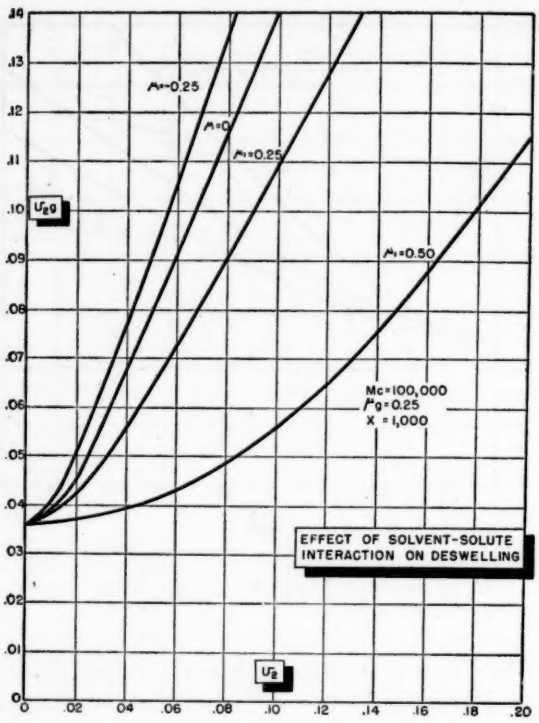

Fig. 5. Effect of μ_1 on deswelling action. By comparison with Fig. 4 it is seen that $\mu_1 \ll 0.5$ and $\mu_g \approx 0.5$ favor deswelling.

established when a swollen gel is transferred from pure solvent to a solute system should be given by equating the activity of the solvent within and without the gel. The solvent will leave the phase in which its activity is higher until this equality obtains. It will be realized that this same equilibrium swelling volume should also prevail if the gel is swollen for the first time in the presence of a solute.

The deswelling action can be seen clearly by examining Fig. 1 which is a plot of solvent activity as a function of polymer concentration. The top curve, referring to the gel phase, and the bottom curve, referring to the solute system, were obtained by substituting numerical values in Eqs. (1) and (3), respectively. The gel is in equilibrium with pure solvent when the activity of the solvent is unity, and hence when v_{2g} is 0.037. If this gel is now transferred to a 4 percent by volume solution of polymer, it will shrink by moving down along the upper curve until the activity of the solvent is the same in both phases, as indicated by the horizontal dotted line. v_{2g} will now be 0.056. In general, for a finite molecular weight of the solute and for μ_1 less than 0.5, the curve for the gel will always be above the solute curve. v_{2g} will always be greater than v_2, although the two curves approach each other and finally meet for $v_2 = v_{2g} = 1$. When μ_1 is larger than μ_g, the activity *versus* concentration curves will intersect for v_2 less than unity. The general condition for this is that $a_1 = a_{1g}$, and $v_2 = v_{2g}$, whence

$$(\mu_1 - \mu_g)v_2^2 = v_2/x + (\rho V_1/M_c)v_2^{\frac{1}{3}}. \qquad (4)$$

Since the right-hand side of the equation must be positive, μ_1 must be greater than μ_g. In case x is extremely large,

$$v_2 = [\rho V_1/(\mu_1 - \mu_g)M_c]^{3/5} \qquad (5)$$

gives the abscissa of the point of intersection. The gel will still deswell under such conditions, although v_{2g} may be greater than, equal to, or less than v_2, depending on the value of v_2. Since $\mu_1 > \mu_g$ is a very unfavorable condition for deswelling, as will be seen presently, this case of intersecting activity curves is of slight practical interest.

To illustrate further the extent of deswelling action, a series of curves shown in Figs. 2–5 have been prepared, using essentially the graphical method indicated in Fig. 1. Certain arbitrary values were chosen for the parameters such as to illustrate cases that might arise in practice. Three gels of different degrees of cross-linking were selected, with $M_c = 10{,}000$, 100,000, and 500,000, and with μ_g ranging from -0.25 to 0.5. ρV_1 was made equal to 100. The soluble polymers were characterized by $x = 100$, 1000, and 10,000. In the case of polystyrene dissolved in toluene this would correspond approximately to molecular weights of 10^4, 10^5, and 10^6. μ_1 ranged from -0.25 to 0.50. The complete expressions for solvent activity (Eqs. (1) and (3)) were employed in these calculations since the expansion of the logarithms would require the use of too many terms in the series, particularly for the gel. In making some of the cross comparisons, a typical polymer was chosen as $X = 1000$, $\mu_1 = 0.25$, while a typical gel was assumed as $M_c = 100{,}000$, $\rho V_1 = 100$, and $\mu_g = 0.25$.

In general we can equate the logarithms of the solvent activities given by Eqs. (1) and (3). If we represent the negative of the right-hand side of

Eq. (1) by the swelling function, $S(v_{2g})$, and if we expand logarithms and combine terms in Eq. (3), we obtain for $\ln a_{1g} = \ln a_1$:

$$S(v_{2g}) = v_2/\bar{x}_n + (0.5 - \mu_1)v_2^2 + v_2^3/3 + +. \quad (6)$$

$S(v_{2g})$ contains the constant quantity, $\rho V_1/M_c$, which can be evaluated numerically from swelling experiments in pure solvent. However, Flory has suggested[17] that if $\rho V_1/M_c$ is replaced by its algebraic equivalent, as given in Eq. (2), then

$$S(v_{2g}) = (0.5 - \mu_g)2v_{2g^0}\Delta + v_{2g^0}{}^2\Delta + +, \quad (7)$$

where v_{2g^0} is the volume fraction of polymer in the gel which is in equilibrium with pure solvent, and $\Delta = v_{2g} - v_{2g^0}$. Substituting in Eq. (7) and rearranging gives

$$\frac{\Delta}{v_2} = \frac{1/\bar{x}_n + (0.5 - \mu_1)v_2 + +}{2(0.5 - \mu_g)v_{2g^0} + v_{2g^0}{}^2/(1 - v_{2g^0})}. \quad (8)$$

This equation predicts that the change in swelling per unit of dissolved polymer is greater when $\bar{x}_n$ and v_{2g^0} are small, $\mu_1 \to 0$, and $\mu_g \to 0.5$. In other words, a very loose or slightly cross-linked gel should be swelled in a medium which is a poor solvent for the network polymer but a good solvent for the solute ($\mu_1 < \mu_g$).

In practice there are physical limitations which dictate to a large extent what gels and solvents may be employed. Gels swollen to 25 or more times their dry volume deform readily and are difficult to handle. Moreover, with poor solvents (large μ_g) loose gels become quite tacky and will rupture easily. Eqs. (6) and (8) nevertheless provide a basis for molecular weight determinations from deswelling experiments. Before discussing this subject there are several interesting questions which should first be considered.

PERMEATION OF SOLUTE INTO THE GEL

In the course of some experimental studies certain discrepancies were noted which suggested that soluble polymer might be permeating into the gel. For instance, a divinyl copolymer originally swelled in toluene for an insufficient time to reach equilibrium was then transferred to a polystyrene solution. Instead of deswelling the sample increased in weight beyond what was predicted as its equilibrium value. On removal of the specimen to pure toluene it deswelled to its correct equilibrium volume.

It is not surprising that polymer molecules, especially those of low molecular weight, could permeate the loose structure of a swollen gel. Physically, however, if the gel deswells on being placed in a solute, the stream of solvent leaving the gel should offset the tendency for polymer to migrate into the gel. Alternately, if a dry gel is swollen for the first time in contact with a solution, then solute could be carried into the gel rather easily. Disregarding such diffusion currents caused by the bulk movement of the solvent, the diffusion of the solute would be relatively slow. Moreover, the concentration of polymer in the gel (in the form of network chains) will usually be higher than the concentration of soluble polymer in the external solution. Thus the effective concentration gradient causing diffusion of solute molecules might be extremely small.

Fortunately Flory[17] was able to provide a positive statement concerning the effect of such permeation on the swelling behavior of the gel, He showed that even if the polymer does enter the gel, its influence on swelling will be negligible except when the molecular weight of the solute is extremely low and/or when the degree of swelling is extremely high. Specifically, this effect can be neglected if (x/V_0) is greater than 5. x is again the volume ratio of polymer to solvent molecule, and V_0 is the swelling volume $(=1/v_{2g})$ in pure solvent. Since V_0 would likely never exceed 50 because of difficulties in handling such loose gels, this criterion sets a limit of $x = 250$, corresponding roughly to a molecular weight of 25,000. Actually, the smaller the molecular weight of the polymer, the smaller can V_0 be and still furnish good sensitivity. In practice then, this restriction is not a severe one. If, however, a weighing method is used, the extra weight of the solute in the gel would contribute a minor error.

We have referred thus far to the deswelling action of high polymer solutes. Any solute which lowers the activity of the solvent will show this

[17] I am indebted to Dr. Flory for the privilege of discussing this problem with him, and for his subsequent derivation of several equations which are used here with his permission.

deswelling action initially. Eventually, however, a low molecular weight solute would permeate the gel and the problem would reduce to one of mixed solvents. It seems convenient to choose Flory's critical condition, $(x/V_0)>5$, as a definition of the type of solute with which we are here concerned. Flory has suggested, in the case of a heterogeneous polymer, that even though the average sized molecule will not cause trouble by permeation, yet some of the smaller species present may do so. This is a selective effect which might be likened to the diffusion of low molecular weight species through the membrane in an osmotic pressure experiment.

Another possible disturbing influence might be the effect of hydrostatic pressure on the swelling volume of these gels. All of the experiments reported here were carried out with a small head of solvent (approximately 5 cm). At equilibrium swelling, the swelling pressure (defined by Posnjak[18] as the pressure needed to prevent further swelling) is zero. Hence weak gels should be quite sensitive to small changes in pressure under conditions of a deswelling experiment. Preliminary experiments on gels swelling 20-fold in toluene showed a slight decrease in swelling volume as the head of liquid was increased from 1 to 100 cm. For most purposes this effect can be neglected.

Thus far we have stressed the use of cross-linked gels for this work. The soluble type of gels mentioned in the introduction should also offer some possibilities for investigation. Bronstead and Volqvartz, for example, have studied the swelling of polystyrene in alkyl laurates.[19] This system is characterized by large values of μ_1.[7] Polymers for which the alkyl laurates are good solvents (μ_1 small) would be expected to deswell these polystyrene-alkyl laurate gels. Here the action would not arise from a tendency for network contraction, but would result largely from heat of dilution effects as expressed in experimental values of μ_g and μ_1. Gee's theory of swelling would be applicable here.[3] Such a system would be subject to more experimental restrictions in choosing solvents, than is the case with a cross-linked gel.

MOLECULAR WEIGHTS OF HIGH POLYMERS FROM THE DESWELLING OF GELS

This present investigation of gels was prompted by a search for new methods of measuring molecular weights of polymers. It was inspired, not by the work of Blow and Stamberger which was unknown to us at the time, but by some biological considerations. Briefly, it is believed that the mechanism through which simple salt solutions destroy bacteria is an osmotic dehydrolysis of the microorganism.[20] This suggested that bacteriocidal action might give a quantitative measure of osmotic pressure. H. deVries, around 1884, was able to compare the osmotic pressure of various aqueous solutions by their action on the structure of plant cells, while Hamberger, in 1886, used red blood cells for the same purpose. Glasstone has recently called attention to both of these techniques.[21] Aside from the possible restriction of such methods to aqueous systems, it seemed doubtful if an absolute measure of the osmotic pressure could be obtained. A cross-linked polymer, swellable in organic liquids, scientifically reproducible, large enough to be handled and weighed with precision, and finally, as we have seen, amenable to mathematical investigation, presented itself as a substitute for bacteria or plant cells or red blood corpuscles. The theoretical treatment given above, and some experimental results which will now be presented, show that it is possible, both in principal and in performance, to measure molecular weights of polymers by the osmotic deswelling action of their solutions.

For this purpose we divide Eq. (6) by v_2 and transpose one term to give:

$$S(v_{2_0})/v_2 - v_2^2/3 = 1/\bar{x}_n + (0.5-\mu_1)v_2 + + + . \quad (9)$$

This equation implies that if gel samples are swelled to equilibrium in pure solvent and then transferred to several solutions of polymer at different concentrations in the same solvent, the

[18] E. Posnjak, Kolloidchem. Beihefte **3**, 417 (1912); see also P. J. Flory and John Rehner, Jr. "Effect of Deformation on the Swelling Capacity of Rubber," J. Chem. Phys. **12**, 412 (1944).

[19] J. N. Bronstead and K. Volqvartz, Trans. Faraday Soc. **35**, 576 (1939).

[20] R. E. Buchanan and E. I. Fulmer, *Physiology and Biochemistry of Bacteria* (Williams and Wilkins, Baltimore, 1930), Vol. II, p. 195ff.

[21] Samuel Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1940), p. 651–3.

TABLE I. Deswelling of 0.033 percent divinylbenzene—styrene gels by toluene solutions of polystyrene at 24°C.

Gel no.	Maximum weight ratio in pure toluene[a]	Stabilized weight ratio in pure toluene[b]	Volume concentration of polystyrene[c] v_2	Corrected weight ratio in solution[d]	v_{20} [e]	$\frac{V_1}{\rho M_c}\times 10^6$	$S(v_{20})\times 10^7$	$\frac{S(v_{20})}{v_{20}}-\frac{v_2}{3}$ $\times 10^5$
236	20.58	18.11	0	20.10	0.0414	368		
239	20.71	18.11	0.00475	19.79	0.0420		33	69.5
241	20.79	18.10	0.00946	19.27	0.0432		107	110
243	20.52	18.05	0.0141	18.45	0.0451		227	154
252	20.51	18.05	0.0187	17.60	0.0473		379	191
246	20.53	17.94	0	19.92	0.0420	375		
237	20.51	17.97	0.0231	16.35	0.0510		631	255
233	20.30	17.92	0.0276	15.46	0.0540		880	294
244	20.41	17.84	0	19.71	0.0421	378		
250	20.21	17.88	0.0318	14.26	0.0585		1285	368
249	20.63	17.89	0.0361	13.40	0.0623		1677	422
240	20.51	17.77	0.0447	12.38	0.0676		2287	445

[a] Based on original dry weight of gels (approximately 0.27g).
[b] After leaching gels for 4 months in toluene at 24°C.
[c] Corrected for dilution by toluene from gels.
[d] Calculated from weight swelling ratio in solution after assuming that gels had lost 10 percent of their original weight as soluble material.
[e] Volume fraction corresponding to corrected weight ration in solution.
Note: Swelling was followed by removing sample from solvent or solution, rolled gently on Whatman Filter Paper no. 3, and weighed in a weighing bottle.

resultant deswelling data can be so handled as to yield a straight line permitting an accurate extrapolation to infinite dilution of the solute. The slope of this line measures the interaction, μ_1, between solvent and solute. The intercept of this line is inversely proportional to the number average volume ratio, $\bar{x}_n$, between solute and solvent molecules. Hence it is inversely proportional to the number average molecular weight, $\bar{M}_n$

$$\bar{M}_n = \bar{x}_n V_1 d_2,$$

where V_1 is again the molal volume of the solvent and d_2 is the density of the solute. The general agreement in form between Eq. (9) and the extrapolation method successfully employed for osmotic pressure measurements[15] is complete in every detail, except for some obvious numerical constants. Eq. (8) also furnishes a method for extrapolating deswelling data to infinite dilution. We shall employ Eq. (9) later because it involves no approximations other than those implicit in Eqs. (1) and (3).

Deswelling experiments therefore appear to offer a relatively convenient method of determining molecular weights of polymers. This technique is simply a variation of the osmotic pressure method. The swollen gel acts in effect like the membrane in an osmometer, allowing solvent molecules to diffuse freely through while retarding at least the larger polymer molecules. Contrary to usual osmotic experiments, the solvent moves from the more concentrated to the more dilute system (except for some special cases mentioned earlier). Moreover, the "membrane" has a definite interest in how many solvent molecules are transported, the extent of this interest being expressed by the two characteristic gel constants M_c and μ_g. M_c is known from a single swelling measurement according to Eq. (2); μ_g is found from swelling measurements at several temperatures through the use of Eq. (15′) of reference 6, or from swelling experiments in a solution of known activity.

A number of experiments have been carried out in an effort to verify Eq. (9). These experiments have served mainly to emphasize two disturbing properties of slightly cross-linked gels. The first is that a series of supposedly identical dry gel samples do not swell to the same extent in pure solvent. The variations encountered are greater the smaller the amount of cross-linking agent present. As one example, 20 identical samples containing 0.033 percent divinylbenzene showed equilibrium weight swelling ratios in toluene ranging from 19.15 to 20.98 times the dry weight, with an average value of 20.43. The second difficulty is that these gels contain an appreciable amount of soluble polymer which

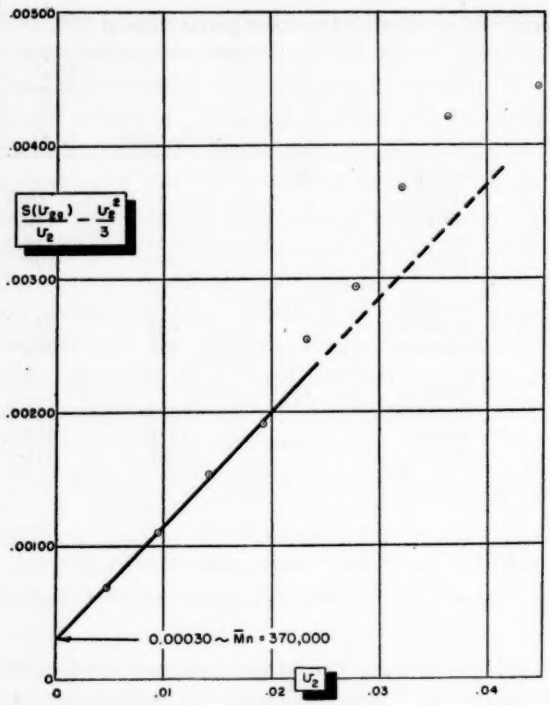

FIG. 6. Application of Eq. (9) to the deswelling of 0.033 percent divinylbenzene-styrene copolymer gels by toluene solutions of polystyrene having an osmotic pressure molecular weight of 300,000.

leaches out with time. Staudinger has already noted this fact, pointing out that the amount of soluble material increases with decreasing divinylbenzene content.[8] In some cases 50 to 60 percent of soluble polymer was recorded. An obvious expedient has been to start with a large number of samples, leave them in toluene until the weight has passed through a maximum and then decreased to a constant value, and finally to choose from this group the few needed samples which are reasonably close together in swelling ratio. Several changes of solvent are required so that the soluble polymer will not influence the swelling ratio. Only then should the gels be transferred to high polymer solutions for deswelling observations.

Table I presents some deswelling data obtained on gels that were so treated. Out of 20 original samples it was not possible to find the required 10 whose stabilized weights were sufficiently close. Three groups of samples, each with an appropriate blank, were finally transferred to toluene solutions of polystyrene. Column 2 lists the maximum weight swelling exhibited by these gels in pure solvent, while column 3 is the stabilized weight ratio after most of the soluble polymer had been removed by toluene. v_2 is the volume fraction of polystyrene in solution, after correction for dilution by the toluene which left the gels during deswelling. v_{2g} is the volume fraction of polymer in the deswollen gels. In calculating v_{2g} it was assumed that the original sample weight had decreased by 10 percent through loss of soluble material. This is admittedly a crude approximation based on the fact that the stabilized weight ratios are about 10 percent less than the maximum weight ratios, and on the assumption that the soluble polymer while still in the gel was swollen approximately 20 times. A more exact treatment for the effect of soluble polymer is evidently needed. The remaining columns of the table show the calculated quantities needed to compute a molecular weight. μ_g was again assumed to be 0.44, while the density of the dry gel was taken as 1.05. Figure 6 is a plot of this data according to Eq. (9). The extrapolated value for $1/\bar{x}_n$ is 0.00030, thus indicating a number average molecular weight of 370,000 for the polystyrene. Osmotic pressure measurements in methyl *n*-amyl ketone gave a molecular weight of 300,000 for this same polymer, while light scattering measurements indicated 302,000. From the slope of the line,

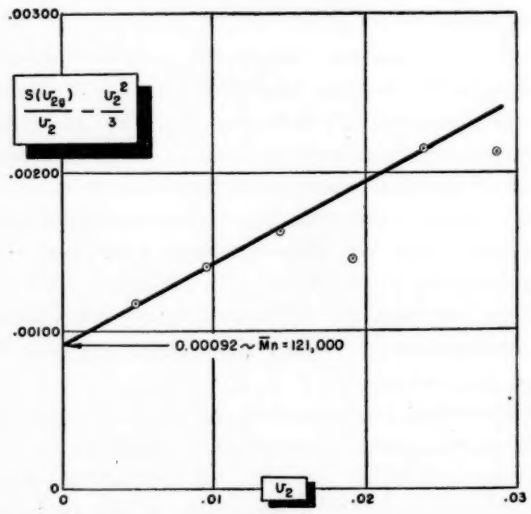

FIG. 7. Application of Eq. (9) to the deswelling of 0.0462 percent divinylbenzene-styrene copolymer gels by toluene solutions of polystyrene having a molecular weight of 115,000 by light scattering.

μ_1 is 0.42. This is lower than the value of 0.44 given by Huggins,[7] or the several values listed by Mark.[9] This particular polystyrene had been prepared in mass without catalyst at 100°C.

The first four points of Fig. 6 lie exactly on a straight line, while the points for more concentrated solutions depart from this line in a way which suggests an upward curvature. Similar curvature in osmotic pressure curves has been observed.[9,22] The points which are off the curve had different swelling ratios in pure solvent than the first four points, as can be seen in the table. In one other example, shown in Fig. 7, toluene solutions of a polystyrene prepared by emulsion polymerization at 80°C were used to deswell a series of gels containing 0.0462 percent divinylbenzene. The number average molecular weight from the deswelling data was 121,000, compared with a light scattering molecular weight of 115,000. μ_1 came out as 0.45. These gels swelled in toluene to approximately 12 times their dry weight, and contained less soluble matter than the 0.033 percent gels. In both cases uncertainty exists because of our assumption that $\mu_0 = 0.44$, and because of soluble constituents in the gels. In general these two sets of measurements appear to confirm the theory. However, a series of narrow polymer fractions of known molecular weight should be measured on one series of gels, and cross-checked on gels of different swelling power, and with different solvents before the general validity of the method can be assessed.

DISCUSSION OF THE METHOD

Because of limited experience, it is obviously impossible at the present time to offer a critical evaluation of this gel method of measuring molecular weights of high polymers. There are, however, some general considerations which might be discussed for and against the method.

1. The simplicity of the method is its most striking feature. It is possible to have dozens of gels available for use at any time.

2. The accuracy in measurement characteristic of any method employing an analytical balance is potentially available here. Julander and Svedberg[23] have already shown that the accuracy of osmotic pressure measurements can be increased tenfold by use of a weighing technique. Some osmotic pressure methods involve an uncertainty of 10 percent for $\bar{M}_n$ of 70,000 which increases to 50 percent at $\bar{M}_n = 225{,}000$.[24] More precise results have been obtained.[25] It is difficult to assign an uncertainty figure for the gel method, but at the present time it is likely no better than osmotic pressure techniques.

3. These gels can probably be used at elevated temperatures to measure difficult soluble polymers. Polyethylene does not show much solubility below 70°C, while polyvinylidene chloride is usually studied by viscosity in *o*-dichlorobenzene at 120°C. The latter polymer in particular defies any existing method of absolute molecular weight determination. There is a possibility for depolymerization of the gel network at high temperature.

4. A long time is required for these gel samples to reach their equilibrium deswelling value. This can be off-set in part by having a large number of gels in use, so that the total data obtained over a given time will be appreciable.

5. Mildly cross-linked gels are not ideal in their behavior, as mentioned before. Variation in swelling ratio of identical gels, and loss of soluble constituents are the principle disadvantages. Some gel samples swell in peculiar fashion with small protuberances or depressions. Experience in preparing gels may show how to eliminate these faults. Divinylbenzene monomer is probably far from ideal because it polymerizes more readily than styrene, and may be totally consumed before completion of polymerization. This would lead to excessive soluble matter. A system like methyl methacrylate-glycol dimethacrylate may give a more homogeneous gel.

6. The numerical calculations involved in applying Eq. (9) are tedious although the work required can be lessened by the construction of special charts and tables. Eq. (8) is somewhat simpler to manipulate.

7. Finally, there is some question about the absolute accuracy of the thermodynamic theory of high polymer-solvent systems. Flory has been critical of the theory, pointing out that it holds

[22] M. L. Huggins, Ind. Eng. Chem. **35**, 980 (1943).
[23] I. Julander and T. Svedberg, Nature **153**, 523 (1944).
[24] R. H. Wagner, Ind. Eng. Chem. Anal. Ed. **16**, 520 (1944).
[25] P. J. Flory, J. Am. Chem. Soc. **65**, 372 (1943).

better for concentrated solutions than for the dilute solutions of interest here. He has attempted to correct this situation.[26] Flory has also emphasized that three-dimensional polymers are usually not perfect networks, but contain many loose chain ends which do not contribute their full share toward swelling equilibrium. He has indicated a method of correcting for this.[27] This same article contains a curve showing excellent correlation between swelling of vulcanized rubber samples in pure solvent, and the modulus of elasticity of the dry gel at 300 percent elongation. Such data indicate that the Flory-Rehner theory of swelling is essentially correct.

[26] P. J. Flory, paper presented at the Pittsburgh meeting of the American Chemical Society, September, 1943. See also W. J. C. Orr, Trans. Faraday Soc. **40**, 320 (1944); T. Alfrey and P. Doty, J. Chem. Phys. **13**, 77 (1945).

[27] P. J. Flory, Chem. Rev. **35**, 73 (1944).

ACKNOWLEDGMENT

I should like to express appreciation here to Dr. P. R. Wenck for several discussions on the biological aspects of osmotic pressure; to my wife for the detailed numerical calculations required for Figs. 1 through 5; to Dr. P. J. Flory for critical comments and valuable suggestions concerning the method; and to Dr. J. J. Grebe who has consistently encouraged interest in new methods of determining molecular weights and molecular weight distributions on high polymers.

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The Adsorption of Gelatin to Silver Bromide*

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Experimental data are presented illustrating a *specific case* of amphipathic adsorption, namely, of gelatin to silver bromide. In this there is mutual coagulation of the silver hydrosol and protein, followed by peptization in excess of dissolved protein. The phenomena in their relation to the isoelectric point of the protein and the *p*H of the solution are interpreted in terms of a basically duplex polar : non-polar structure in proteins, and of a resonance factor, involving both adsorbent and adsorbate, in similar cases.

IN previous work[1] it was observed that:

(i) At *p*H 6.5 and 50°C washing left a constant residual amount of gelatin on silver bromide grains from a photographic emulsion, in the specific case, about 3.4 mg per g. There was but slight change between *p*H 4 and *p*H 10.

(ii) By digesting with boiling water, the amount retained was reduced to about one-half.

(iii) From the photomicrographically determined grain size-frequency the surface area of the grains could be obtained. From this, and taking a value *ca.* 8A for the thickness of a monomolecular layer of gelatin, it could be concluded that the gelatin was held primarily in a monomolecular layer, with a secondary layer attached by weaker forces.

Subsequently, it was noticed[2] that Zsigmondy has recorded that gold foil dipped in gelatin solution retained a small amount of gelatin not removed by boiling water. Our more recent** experiments have been carried out with silver bromide hydrosols, prepared with a slight excess of bromide ion. A standard sol was prepared, usually in a quantity of 4 liters, as follows: 200 ml of 0.40*N* $AgNO_3$ and 200 ml of 0.440*N* KBr were run simultaneously into 3600 ml of distilled water continuously stirred. The bromide

* Communication No. 1038 from the Kodak Research Laboratories.

[1] S. E. Sheppard, R. H. Lambert, and R. L. Keenan, J. Phys. Chem. **36**, 174 (1932).

[2] R. Zsigmondy, translated by E. R. Spear, *The Chemistry of Colloids*, Part I (O. Spamer, Leipzig, 1912), p. 112. "As early as 1900 the author (R. Zsigmondy) demonstrated that gold foil adsorbed gelatin and covered itself with a layer that could not be removed by boiling water. This layer prevented the amalgamation of the gold with mercury."

** This work has been repeatedly interrupted by pressure of war work.

solution was run in slightly ahead of the silver, to assure a continual excess of bromide ion. The final sol had 0.002*N* excess bromide ion. Subsequent measurements of specific surface by dye adsorption indicated a 21 percent drop of surface in three weeks.

The surface determinations were made with a solution 5.3×10^{-4} molar of Dye IVb (3,3'-diethyl-9-methyl thiocarbocyanine bromide) in ethyl alcohol, using slight modifications of our previously described technique.[3] Varying titers of this solution were introduced into 50 ml glass stoppered centrifuge tubes, plus enough alcohol to give 4 ml. Fifteen ml water were added to each tube followed by 25 ml of the solution. The tubes were tumbled for ½ hour and then centrifuged ½ hour in an International Centrifuge, Size 1, Type SB. This was kept heated to 40°C ∓1°C. Operations with the silver bromide were carried out under a No. 0 Wratten safelight.

It was originally hoped that the sol particles could be separated centrifugally at any stage of addition of gelatin solution, allowing the residual gelatin concentration to be determined. In that case regular adsorption isotherms, as plots of x/m *vs.* C_r would be obtained. Actually, any separation was very imperfect, and all that was established was, at first, progressive precipitation of silver bromide, with more or less complete removal of the gelatin from solution, until the precipitate commenced to redisperse so that no definite separation could be effected. But the redispersed silver halide carried up gelatin with it, since the whole fluid showed itself enriched in gelatin. The analytical results could be schematically expressed by Fig. 1, but the value of x/m at which, on further gelatin addition, this began to appear in the supernatant liquid, could not be determined with exactitude, varying, for example, from 0.005 mg to 0.008 mg.

Pending development of analytical methods permitting precise determination of adsorption isotherms, a photometric method of following the precipitation *cum* repeptization cycle was developed which lends itself to much exploratory work in this field, and rather clearly indicates the character of the phenomenon. Gelatin solutions of known concentrations were prepared, corrected to dry weight of gelatin. Appropriate

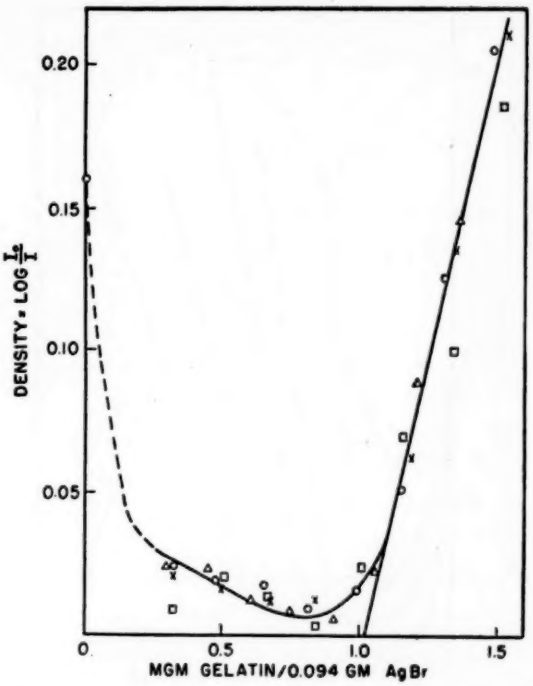

FIG. 2. Reproducibility of reaction of gelatin with AgBr sol. ○ = 5½ hours shaking; × = 5½ hours shaking; △ = 2 hours shaking; □ = 2 hours shaking.

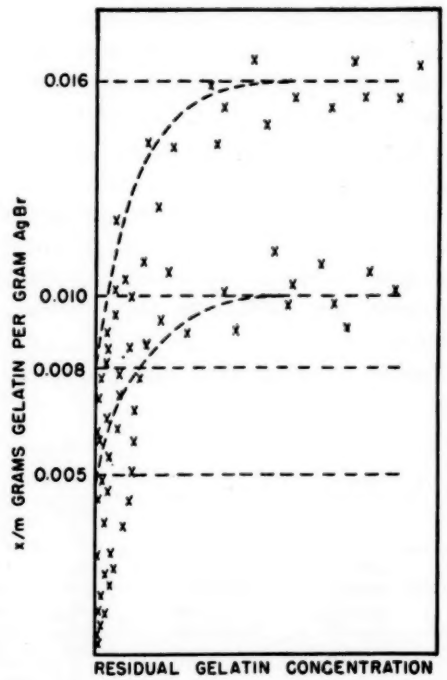

FIG. 1. Schematic isotherm of adsorption of gelatin to silver bromide.

[3] S. E. Sheppard, R. H. Lambert, and R. D. Walker, J. Chem. Phys. 7, 265 (1939).

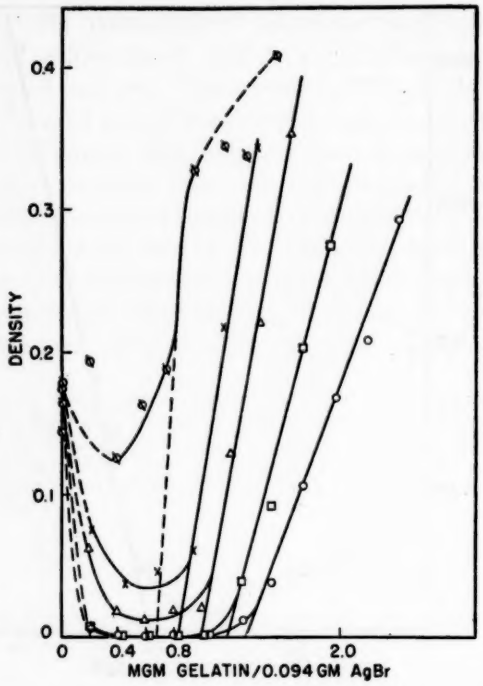

FIG. 3. Effect of molecular weight on adsorption of gelatin to AgBr. ⊘=20,000 m.w.; ×=43,000 m.w.; △=46,000 m.w.; □=70,000 m.w.; ○=110,000 m.w.

amounts were introduced into centrifuge tubes, and enough water to make up to 15 ml. The tubes were brought to 40°C in a water thermostat, and 25 ml of sol added to each tube, and they were shaken for periods varying from 10 minutes to 5½ hours. On removal from the bath they were centrifuged at 40°C for 30 minutes, then 25 ml of the supernatant liquid withdrawn and photometered.* Short periods of shaking were found inadequate but good reproducibility was obtained with 5 to 5½ hours. Figure 2 shows results, for a deashed, Eastman Kodak gelatin No. 148 with some values at 2 hours, which are less concordant; 3 to 4 hours seems sufficient.

FRACTIONATION OF GELATIN

A deashed Eastman Kodak gelatin No. 127 was separated into a number of fractions, the molecular weights of which were determined by osmotic pressure and viscosimetry. The results of a comparison are shown graphically in Fig. 3.

It may be noted that (i) the fraction of highest molecular weight precipitates the sol most completely, and, consistently with this observation, the precipitation declines somewhat with lower molecular weight, so that indeed, the fraction of lowest molecular weight showed little effect and (ii) the amount of gelatin, by weight, able to saturate the surface of unit weight of AgBr decreases steadily with decreasing molecular weight.

From the specific surface of AgBr corresponding to 25 ml of sol, determined for the day of experiment by the dye coverage procedure, the average areas "occupied" by one molecule of each fraction were calculated (Table I).

A graph of surface covered per "molecule" is shown in Fig. 4.

This is reasonably linear, though there is no evident reason why the line should not pass through the origin, since no "reservation not to be populated" can be assumed. As an initial approximation, it can be deduced that the molecules lie "flat" on the surface. Recent investigations by Scatchard *et al.*[4] led them to the conclusion that the dispersed molecules of gelatin in aqueous solution were on an average not longer than 1000A. While it is not believed that the absolute values obtained for the molecular weights of our gelatin fractions are to be regarded as very exact, it is felt that the relative values are reliable. At the same time, if the width of the chain molecule were of the same order as that of the thickness deduced from spread film measurements,[5] namely, about 8–9A, the *areas per molecule* found would not be in conflict with the conclusion of Scatchard and his collaborators.

It should be noted that the end point for

TABLE I.

Mol. wt.	Grams gelatin covering 25 HCl sol	Surface area of 1 g of AgBr in cm²	Area per molecule of gelatin in A²	Δ Thickness in A
110,000	0.00132	6.02×10^{4}	7800	17.3
70,000	0.00120	5.93×10^{4}	5400	14
46,000	0.00101	5.74×10^{4}	4100	14
43,000	0.00085	5.65×10^{4}	4400	12
20,000	0.00070	6.20×10^{4}	2700	9

* Using an Eimer and Amend photronic photometer, with a green-light filter.

[4] G. Scatchard, J. L. Oncley, J. W. Williams, and A. Brown, J. Am. Chem. Soc. **66**, 1980 (1944).

[5] R. L. Keenan, J. Phys. Chem. **33**, 371 (1929). E. Gorter and F. Grendel, Trans. Faraday Soc. **22**, 477 (1926).

coverage is not too well defined. In the first calculations it was taken as the *point of redispersion* or repeptization, but a lower value than this will be discussed.

By assuming that the *density* of the first monolayer of gelatin is the same as for anhydrous gelatin in mass, *viz.*, 1.34, there can be calculated from the figures for molecular coverage the corresponding monolayer thickness Δ. A revised figure, Δ′, for this is obtained by considering that not the "point of redispersion," but the point of "maximum precipitation," as equivalent to the mid-point, gives the true value for monolayer adsorption, whence Table II.

Although the accuracy does not warrant an expectation of Δ nearer than 2∼3A, it is believed that the closer approximation of Δ′ to the value from spreading experiments indicates that the estimation of the end point as the minimum is a better approximation to the true "turning point" or end point.

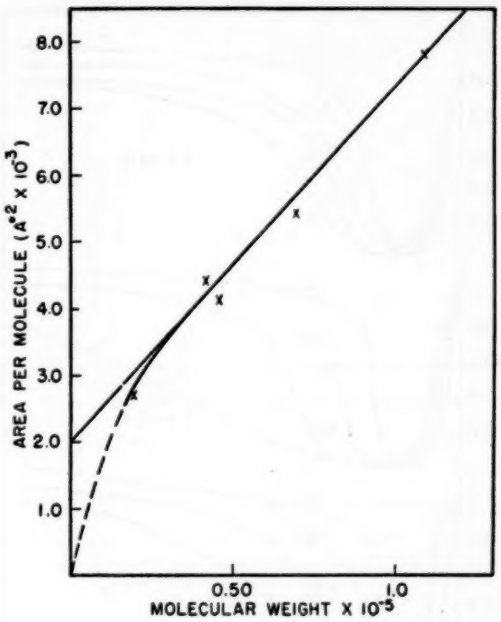

FIG. 4. Relation of area covered to molecular weight.

OBSERVATIONS ON TYPE OF GELATIN AND EFFECT OF *p*H

Some preliminary observations have been made on the influence of the type of gelatin (unfractionated) and on the effect of *p*H. These observations are evidently liable to considerable uncertainty, since the samples were not fractionated. However, the differences produced by the factors mentioned appeared to be of a subsidiary character. The four gelatins differed as shown in Table III.

Figure 5 shows the relative cycle of amphipathy of these gelatins to silver bromide sol, where by *amphipathy* is here meant presence of both hydrophile and hydrophobe properties, as shown in the over-all cycle of precipitation (agglutination) and dispersion (repeptization). There does not appear to be any fundamental difference produced either by change of *p*H (of the solution) of one and the same gelatin, or between *different* gelatins, that is, differing as to source and treatment. It has been shown[6] that the process of plumping, whether merely acid, or fundamentally alkaline, determines the isoelectric point. While the general contour of the cycle does not appear changed, it may be noticed that the width between the branches of the curve appears to depend upon these factors. This is brought out in the graph of Fig. 6, which indicates as ordinate the range of gelatin concentration giving the same relative stability, as indicated by 0.5 *D* in Fig. 5. It will be noticed that there is a tendency for this to be maximal at the isoelectric point of the gelatin used, and

TABLE II.

Area mol.	End point as redispersion	Δ Thickness in A	End point as minimum (estimated)	Δ′ Thickness in A
110	1.35	17.3	0.80	10.0
70	1.20	14.0	0.70	8.2
46	1.02	14.0	0.60	8.2
43	0.85	12.0	0.70	10.0
20	0.68	9.0	0.40	6.0

TABLE III.

Gelatin	Source	Treatment	*p*H of isoelectric point
1	Isinglass	Weak acid plumping, not deashed	9.12
2	Sharkskin	Lime-plumped, deashed	4.90
3	Pigskin	Plumped in NaOH, deashed	5.40
4	Pigskin	Lime-plumped, not deashed	4.90

[6] S. E. Sheppard and J. H. Hudson, U. S. Patents 2,101,877 (1938) and 2,191,034 (1940).

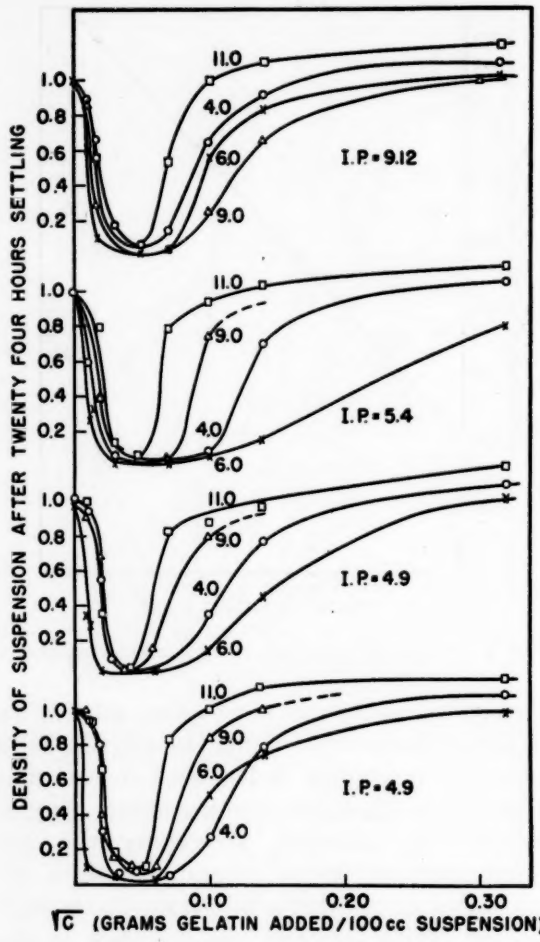

FIG. 5. Adsorption of gelatin of varying origin to AgBr. Numbers indicate *p*H at which experiments were carried out. I. P. is isoelectric point.

to approach about equally low values at very high and low *p*H values. Compare also Fig. 7 for *p*H = 11.0. These results indicate that the adsorption of gelatin does not depend primarily upon its ionization, but upon a more fundamental structural or constitutional property. In the case of dyes, this property, connecting the resonance structure of the dye molecule with that of the silver halide crystal, is exhibited by the shift of the absorption spectrum from that of the independent gaseous dye molecule, and which was large in the case of the non-ionized merocyanine dye.[7] How fundamental it is, is indicated by the phenomenon of optical sensitizing;[8] in the case of gelatin, by such observations as that of Zsigmondy.

[7] S. E. Sheppard, R. H. Lambert, and R. D. Walker, J. Chem. Phys. **9**, 112 (1940).

DISCUSSION

The precipitation of silver bromide sol by gelatin in dilute solution is an aspect of the phenomenon known as the "sensitizing" of colloid coagulation by electrolytes. In the present case where the protective ion is the bromide ion, there was little evidence of displacement of bromide ion by the gelatin on progressive precipitation and adsorption of gelatin. Since precipitation took place with only secondary effects of *p*H, it appeared that it is not simply a matter of neutralization of electric charge. Together with the consequent repeptization by addition of further gelatin beyond the zone of minimum stability, the behavior is consistent with the explanation which we have already given for the same type of process with basic dyes adsorbed to silver bromide. We suppose that the polar surface of the silver bromide adsorbs polar groupings of the gelatin, until the surface is covered with a gelatin layer having its polar groupings directed to the solid, and having relatively hydrophobe, hydrocarbon groups directed outward. As these ectodermal groups meet and cohere, the material is agglutinated and precipitated. On further addition of free

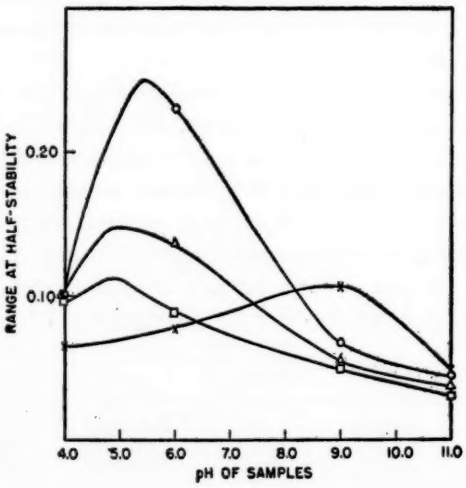

FIG. 6. Effect on the range at half-stability, of the isoelectric point and the *p*H for differing gelatins. × = 9.22 I.P.; ○ = 5.40 I.P.; △ = 4.9 I.P.; □ = 4.9 I.P.

[8] S. Natanson, Nature **140**, 197 (1937).

gelatin in solution, these new molecules are able to attach themselves by *their* hydrophobe groups to the primary monolayer, forming a second monolayer with its polar hydrophile groups directed outward into the aqueous solution. Thus, the redispersed particles are again hydrated and dispersed.

This explanation, though no doubt incomplete, is not only in agreement with our observations on the adsorption of basic dyes, but also with those made previously on the flocculation and deflocculation of silver halides by electrolytes.[9] It was adumbrated by one of us many years ago in connection with several aspects of protein behavior,[10] and, as has been pointed out recently,[11] accounts for the otherwise paradoxical fact that solid particles coated with protein behave cataphoretically as if exposing an amphoteric protein surface,[12] although just such groupings must be engaging the solid surface with powerful polar forces.

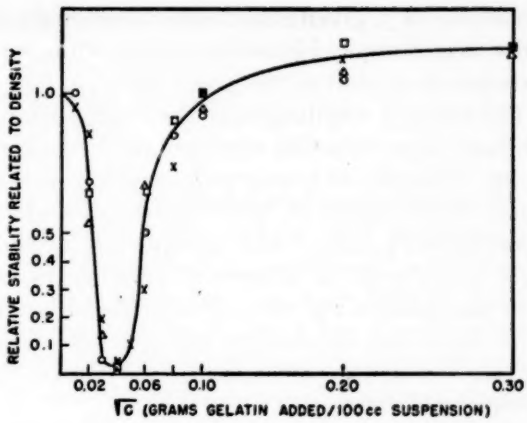

FIG. 7. Behavior of different gelatins at pH = 11.0.

[9] S. E. Sheppard and R. H. Lambert, *Colloid Symposium Monograph*, No. 4, p. 281 (1925).
[10] S. E. Sheppard, Nature **107**, 73 (1921); also "Gelatin in Photography," Monograph No. 3 on the *Theory of Photography* (Eastman Kodak Company and D. Van Nostrand Company, Inc., New York, 1923), p. 189.
[11] S. E. Sheppard, Nature **155**, 266 (1945).
[12] H. A. Abramson, *Electrokinetic Phenomena and Their Application to Biology and Medicine* (Chemical Catalog Company, New York, 1934).

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On the Product Rule

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WHENEVER the symmetry of a molecule is *changed* by the replacement of one or more atoms by their isotopes, it has been commonly considered that the product rule[1,2] applied only to the product of all the $3N-6$ frequencies of molecular vibration.[3] In an excellent book just published, however, Herzberg[4] has indicated how the product rule may be applied separately to certain groups of frequencies of such a molecule. Since this is the first time such an application has been made, to the best of this author's knowledge, it seems worth while to demonstrate its general validity. By approaching the problem in terms of the kinetic and potential energy matrices recently introduced,[5] questions regarding its application in this form may be answered simultaneously.

The symmetry operations of an isotopic molecule form a sub-group of the point group of the non-isotopic molecule. Consequently, certain degenerate, non-isotopic representations may be no longer irreducible and hence split into several representations of the sub-group. In addition several representations may coalesce into one. The result is that each representation of the isotopic sub-group "corresponds to" one or more representations of the group of the non-isotopic molecule. Physically this means that the isotopic

[1] E. Teller, cf. C. K. Ingold *et al.*, J. Chem. Soc. (London) 971, (1936).
[2] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).
[3] Of course when the symmetry is unaltered, the product rule applies to each symmetry type separately.
[4] G. Herzberg, *Raman and Infra Red Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 231.
[5] E. B. Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).

vibrations of a given class have their origin in those non-isotopic vibrations whose symmetry corresponds to that of the given class.

The internal coordinates of the molecule form the basis of a reducible representation of either group. Moreover it is easy to form linear, orthogonal combinations of these coordinates which *simultaneously* reduce *both* groups, and accordingly form a set of symmetry coordinates for both the isotopic and the non-isotopic molecule. With these one obtains for the product of the frequencies of the ath symmetry type of the isotopic molecule[5]

$$\Pi_i\lambda_{ai}=|G_a|\,|F_a|, \tag{1}$$

and similarly for the αth symmetry type of the non-isotopic molecule

$$\Pi_j\lambda_{\alpha j}=|G_\alpha{}^0|\,|F_\alpha{}^0|. \tag{2}$$

Here $\lambda_{ai}=4\pi^2\nu_{ai}{}^2$, ν_{ai} being the frequency and $|G_a|$ and $|F_a|$ are the determinants of the kinetic and potential energy matrices, respectively, of the vibrations of the ath symmetry type. The assumption of the same force field for both molecules combined with the above coordinates yield $F=F^0$. As a consequence F_a will consist of a set of diagonal sub-matrices, one for each of the non-isotopic representations that correspond to the ath isotopic representations. It follows that

$$|F_a|=\Pi_\alpha|F_\alpha{}^0|, \tag{3}$$

and then

$$\frac{\Pi_i\lambda_{ai}}{\Pi_\alpha\Pi_j\lambda_{\alpha j}}=\frac{|G_a|}{\Pi_\alpha|G_\alpha{}^0|}, \tag{4}$$

the symbol Π_α denoting the product over those symmetry types of the non-isotopic molecule which go over to the ath symmetry type in the isotopic molecule. This is the general form of the product rule.

In applying the recently derived form of the *ratio rule*[6] to each separate frequency one uses the above type of symmetry coordinate in setting up the G matrices. The question naturally arises as to the necessity of such a restriction here. Since it is an easy matter to demonstrate that the determinant of a G (and F) matrix remains invariant when a transformation is made from one set of symmetry coordinates to another, the limitation used in developing Eq. (4) is not required. *Any* set of symmetry coordinates may be used for either molecule.

As an example, the effect of replacing one H atom of CH_4 by one D atom will be considered. The molecular symmetry changes from T_d to C_{3v}; the A_1 vibrations of the latter result from the A_1 and T_2 vibrations of the former, while those of symmetry E result from those of symmetry E and T_2. Equation (4) yields

$$\left(\frac{\nu_1\nu_2\nu_3}{\nu_1{}^0\nu_3{}^0\nu_4{}^0}\right)^2=\frac{|G_{A_1}|}{|G_{A_1}{}^0|\,|G_{T_2}{}^0|}, \tag{5}$$

and

$$\left(\frac{\nu_4\nu_5\nu_6}{\nu_2{}^0\nu_3{}^0\nu_4{}^0}\right)^2=\frac{|G_E|}{|G_E{}^0|\,|G_{T_2}{}^0|}, \tag{6}$$

$\nu_3{}^0$ and $\nu_4{}^0$ being the T_2 vibrations, $\nu_1{}^0$ and $\nu_2{}^0$ the A_1 and E vibrations of CH_4. The A_1 vibrations of CH_3D are designated by ν_1, ν_2, and ν_3, while ν_4, ν_5, and ν_6 represent the E vibrations. Making no corrections for anharmonicity, the frequency ratio square in Eq. (5) is 0.56 and the determinant ratio is 0.53; the corresponding quantities of Eq. (6) are 0.75 and 0.72.

This extension of the product rule and the recently developed ratio rule[6,7] provide two new tools for the interpretation of the spectra of isotopic molecules.

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[6] W. F. Edgell, J. Chem. Phys. **13**, 306 (1945).
[7] H. Noether, J. Chem. Phys. **11**, 97 (1943).

Thermodynamics of Linearly Associated Systems

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(Received June 18, 1945)

THE general problem of the thermodynamics of linearly associated systems has received much attention in recent years in connection with the properties of solutions of stable linear polymers.[1-4] The problem of equilibrium size distribution for reversible polymerization-depolymerization has also been treated.[5-7] It is the purpose of this note to indicate the possible applicability of these lattice model methods for the treatment of general thermodynamic problems of reversible association. As example of the types of systems under discussion we may include associated liquids, such as the alcohols, and solutions of associated materials in non-associated liquids, such as the system ethyl alcohol-toluene.

The partition function for a system of the latter kind can be written as

$$Z=f_0^{n_0}f_1^{N}\frac{1}{\sigma^{\Sigma n_x}}\left\{\frac{(n_0+N)!}{n_0!\Pi n_x!}\left(\frac{\gamma}{n_0+N}\right)^{\Sigma(x-1)n_x}\right\}\times b^{n_0+\Sigma n_x}a^{\Sigma(x-1)n_x}\times\exp\left[\frac{\Sigma(x-1)n_xP}{kT}\right]\exp\left[-\mu\frac{n_0N}{n_0+N}\right], \quad (1)$$

where n_0 is the number of unassociated solvent molecules, n_x is the number of x-mers of the associated solute, N is the total number of monomeric units of the associated solute including those incorporated as segments of the x-mers, σ is the symmetry number of the solute molecules, γ is the coordination number of the space lattice, P is the heat of association,* f_0 and f_1 are the vibrational partition functions for each solvent molecule and for each segment (monomeric unit) of solute respectively, μ is a constant characterizing the Van Laar heat of mixing of solvent and solute, and a and b are constants to be discussed later. The factor in Eq. (1) enclosed in curly brackets is the approximate number of distinguishable configurations available to the system for the size distribution specified by the numbers n_0, n_1, $n_2\cdots n_x$, etc., on the basis of the lattice model.[2,3] A very straightforward intuitive method for deriving this factor is given below, although the counting formula must be regarded as approximate.

If every associated solute molecule were broken down into its monomeric segments and if all segments and solvent molecules were distinguishable, the number of configurations on the lattice would be $(n_0+N)!$ In the case of the mixing of associated and non-associated molecules, every solvent molecule and every monomeric solute molecule can go into the lattice in exactly as many ways as previously. Similarly the first segment of every polymeric solute molecule can enter the lattice in exactly as many ways as if it were a monomeric unit. On the other hand the second, third, and higher segments of each polymeric solute molecule has, at most, γ-sites available to it because of being bonded to the immediately preceding segment. Assuming that the number of the γ-sites available to a bonded segment is cut down by the occupancy of previous solvent molecules and segments in the same ratio as is the total number of available sites, each of these bonded segments (second, third, etc.) has exactly γ/n_0+N times as many ways of entering the lattice as if it were a free monomeric unit. The total number of $(n_0+N)!$ configurations available to n_0+N distinguishable monomeric segments is therefore cut down by the factor $(\gamma/n_0+N)^{\Sigma(x-1)n_x}$. The denominator $n_0!\Pi n_x!$ appearing within the curly brackets arises from the necessity of excluding

[1] M. L. Huggins, J. Phys. Chem. **46**, 151 (1942); Ann. N. Y. Acad. Sci. **43**, 1 (1942); J. Am. Chem. Soc. **64**, 1712 (1942).
[2] P. J. Flory, J. Chem. Phys. **10**, 51 (1942); **12**, 425 (1944).
[3] A. R. Miller, Proc. Camb. Phil. Soc. **39**, 54 (1943).
[4] R. L. Scott and M. Magat, J. Chem. Phys. **13**, 172 (1945).
[5] A. V. Tobolsky, J. Chem. Phys. **12**, 402 (1944).
[6] P. J. Flory, J. Chem. Phys. **12**, 425 (1944).
[7] P. J. Blatz and A. V. Tobolsky, J. Phys. Chem. **49**, 77 (1945).
* It appears to us that Flory's criticism (reference 6) of the use of P in reference 5 arises from a misunderstanding of the partition function method.

configurations which are identical save for the interchange of indistinguishable molecules.

The first exponential factor in Eq. (1) involving the heat of association P obviously arises from the assumption of a constant heat of association per bond between segments of the associating solute. The total number of bonds is clearly $\Sigma(x-1)n_x$. The second exponential factor comes from the Van Laar heat of mixing expression.

The factors involving the constants a and b represent a very simplified attempt to account for and characterize entropy changes due to bond formation and due to mixing of holes and molecules, respectively. It is assumed that the formation of each intermolecular bond between the solute segments gives rise to an entropy $k \ln a$ and the mixing of each solute and each solvent molecules with the holes of the liquid gives rise to an entropy $k \ln b$ (if b is equal to e, the base of natural logarithms, this assumption is equivalent to the use of communal entropy).

For simplicity Eq. (1) can be re-written as follows:

$$Z = f_0'^{n_0} f_1'^{N} \frac{(n_0+N)!}{n_0! \Pi n_x!} \left(\frac{\delta}{N+n_0} \right)^{\Sigma(x-1)n_x} \times \exp\left[-\mu(n_0 N/(n_0+N))\right], \quad (2)$$

where $f_0' = f_0 b$ and $f_1' = f_1 b/\sigma$ and $\delta = \beta' e^{P/kT}$ where $\beta' = \gamma\sigma a/b$.

Equations (1) and (2) are the partition function for a system of n_0 solvent molecules and a definite distribution in sizes of associated solute molecules specified by a given set of n_x's. The macrostate corresponding to equilibrium which is characterized by an equilibrium distribution in the n_x's can be calculated by minimizing the free energy obtained from the expression (2). The result of this calculation for the equilibrium distribution gives:

$$n_x = N y^{x-1}(1-y)^2 \quad (3)$$

where

$$y/(1-y)^2 = v_p \delta$$

and

$$v_p = N/(n_0+N).$$

Substituting expression (3) in expression (2) will give the partition function of the macrostate corresponding to equilibrium. The free energy can be obtained as follows:

$$F \cong A = -kT \ln Z. \quad (4)$$

Of particular interest are the partial molar free energies of solute and solvent with respect to the standard states of pure solvent and pure solute, respectively. These differ from the Eqs. (17)–(19) previously given by Flory[6] in that, whereas Flory was considering stable polymer molecules which did not change their size distribution when diluted, we are here concerned with the problem of reversible association which changes with dilution and temperature.

The partial molar free energy of the solvent with respect to the pure solvent as reference state is given by

$$\bar{F}_0 - \bar{F}_{0,N=0} = kT\left[\ln v_0 + v_p y + \mu v_p^2\right], \quad (5)$$

where v_0 is the volume fraction of solvent, and v_p the volume fraction of solute. The symbol y appearing in Eq. (4) is the same as defined in Eq. (3).

The partial molar free energies of the solute species with respect to the pure mixed disoriented solute molecules as the standard state is given by the expression

$$F_1 - F_{1,n_0=0} = kT\left[\ln v_p + \ln \frac{(1-y)^2}{(1-y')^2} + v_p y - y' + \mu v_0^2\right],$$

$$\bar{F}_x - \bar{F}_{x,n_0=0} = kT\left[\ln \frac{y^{x-1}(1-y)^2}{y'^{x-1}(1-y')^2} + x v_p y - x y' + \ln v_p + \mu x v_0^2\right], \quad (6)$$

where

$$y/(1-y)^2 = v_p \delta; \quad y'/(1-y')^2 = \delta. \quad (7)$$

Other reference states, such as the hypothetical pure monomeric solute, are also of interest. Numerical analysis of vapor pressure data and other thermodynamic data are in progress to evaluate the applicability of these ideas to linearly associated systems of the types discussed.

Letter to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

A General Theory of the Reaction Loci in Emulsion Polymerization*

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IN the study of the kinetics of emulsion polymerization no adequate attention had been given to the loci of reaction until the work of this project was begun in January, 1943. On the basis of work by H. F. Jordan and R. H. Ewart on the disappearance of soap early in the reaction, the writer had gained the idea earlier that the principal locus for the *initiation* of polymer particle nuclei is the soap micelles. Very quickly it became evident that there are two types of loci:

A. Loci for initiation of polymer particle nuclei
   1. Soap micelles, and
   2. Monomer droplets
   the relative efficiency of which depends upon the amount of soap and other factors.
B. Locus for formation of most of the polymer
   3. Monomer in the polymer-monomer (latex) particles. Some polymer appears in the emulsion droplets also.

1. LOCUS FOR NUCLEI FORMATION IN THE OIL LAYERS OF SOAP MICELLES

Monomer diffuses continually from the emulsion droplets into adjacent soap micelles, where it forms monomer (oil) layers which polymerize continually. (Fig. 1.) Thus, a layer of isoprene-styrene 16A thick, as shown by x-ray measurements, disappeared (thickness = zero) upon heating in the presence of a catalyst, while the polymer appeared outside in the aqueous phase (R. W. Mattoon and R. S. Stearns). Upon shaking with more monomer the initial *thickness* is restored, though the amount of *micellar* soap has been decreased, as indicated later.

Recently, M. L. Corrin has found that the *apparent* density of heptane solubilized in a soap solution is higher than that of liquid heptane at all concentrations below saturation, but becomes at saturation equal to that of the liquid.

2. MONOMER EMULSION DROPLETS

The evidence that monomer droplets constitute a locus is less direct, but during the two and a half years of investigation of reaction loci considerable evidence, too extensive to be presented here, has been obtained, which shows that they also constitute a locus for the *initiation* of polymer nuclei. These are formed in an emulsion of a monomer in an aqueous solution of an emulsifying agent, even when micelles are absent, and with sufficient agitation slowly even in the absence of any efficient emulsifier.

3. THE LATEX PARTICLES

The latex particles (polymer swelled by monomer) constitute, after their initiation in and escape from the other loci, the locus in which nearly all of the polymer is formed. The monomer of the emulsion droplets diffuses continually through a thin diffusion layer into the adjacent polymer-monomer particles, where it polymerizes continually. In general, the ratio of monomer to polymer in these particles decreases with the yield of polymer.

All hydrocarbon particles (monomer or latex) in an aqueous soap solution are surrounded by an adsorbed monolayer of soap molecules packed with moderate tightness at a soap concentration of 0.1 molar. The polar ends are oriented toward the water and the hydrocarbon ends toward the hydrocarbon particles (Fig. 1). Since the polymer-monomer particles are in general very much smaller spheres than the emulsion droplets, the area on which the soap is adsorbed increases rapidly as the material of the monomer droplets is transformed into monomer-polymer (finally polymer) particles.

As a result the soap of the micelles is rapidly changed into adsorbed soap, so the micelles disappear at a yield (conversion), often rather low, of polymer, which increases with the initial amount of soap present. Above this yield the monomer droplets remain as the only locus for the *initiation* (or formation) of polymer particle nuclei.

At a higher yield the monomer emulsion droplets disappear completely, since the monomer has now diffused wholly into the polymer (latex) particles. Above this yield it is obvious that the only locus of polymerization is

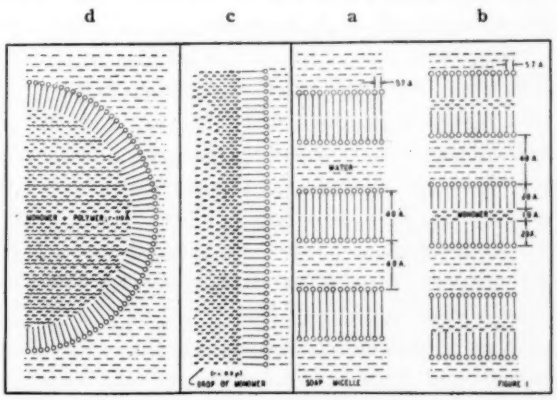

FIG. 1. While the figure is drawn to scale, the actual dimensions vary considerably. The thickness of the water layer increases with decrease of soap concentration, that of the double layer of soap with length of the soap molecule.

a. Idealized structure of a soap micelle,
b. Same with layers of oil, often 15A thick,
c. Monomer droplet: monomer diffuses into micelle, or into
d. Monomer + polymer particle and also gives some polymer at its interface; this usually passes into the aqueous phase.

these latex particles (locus 3). The yield at which the micelles disappear decreases as the initial amount of soap decreases, and this causes the monomer droplets to play a relatively more prominent role in the *initiation* of polymer nuclei.

Since the area of the micellar oil layers increases with the initial amount of soap, the number of polymer particles initiated also increases. Thus, for a given yield the size of these particles decreases as the initial amount of soap is increased, while without soap the particles are in general very large. Much interesting evidence in favor of these concepts has been obtained by others not mentioned above: Dr. W. Heller, H. B. Klevens, B. Adinoff, and H. Oppenheimer.

This outline is far from a complete description of the theory.

* The work reported in this paper was done in connection with the Government Research Program on synthetic rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.